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XX.—CRITICAL DISCUSSION OF THE DETERMINATIONS OF THE
MECHANICAL EQUIVALENT OF HEAT.

By Professor T. H. LABY, *M.A., Sc.D., F.Inst.P.*, University of Melbourne.

Received December 11, 1925.

ABSTRACT.

The principal recorded determinations of the mechanical equivalent of heat are critically discussed, and an attempt is made to correct them for errors not fully taken into account at the time when they were made. The results are weighted according to the relative importance attached to them by the author, and the weighted mean is given as 4.184 joules per calorie at 20 degrees.

THE value of the mechanical equivalent of heat has been critically discussed by Ames,* Luther and Scheel,† and E. H. Griffiths.‡ Since the publication of their articles further determinations of the mechanical equivalent have been made, and the ohm (106.3 cm. of mercury) is now known not to be exactly 10^9 electromagnetic units, as has been assumed in the past. Mr. E. O. Hercus and the writer have been engaged for a number of years upon a direct determination of J ,§ which has required the earlier work to be carefully studied.

It is important to distinguish between the direct determinations of J and the indirect determinations by electrical methods, which yield what might be called the electrical equivalent of heat. Results by the two methods are only comparable in so far as the absolute values of the electrical standards (i.e., the E.M.F.s of the Clark and Weston cells, the mercury ohm, etc.) are known in terms of the corresponding electromagnetic units. So much attention has been given to the electrical units that they are now accurately known (to better than 1 in 10,000), and probably the accuracy with which they are known is more than ten times the accuracy with which J is known by direct experiment.

In arriving at the most probable value of J it is unavoidable that a weight should be given to each result, and there can be no doubt that certain determinations are more accurate than others, and the least accurate should not be given the same weight as the most accurate. Unequal weights are given below, but it is admitted that those given are arbitrary. In order that some judgment may be formed as to the accuracy of the various experiments they are briefly discussed.

Direct Determinations.—There are only two investigations of accuracy. Of Rowland's (1880) investigation, Ames says the "method of taking thermometric readings is liable to serious error." In the light of experiments made by Mr. Hercus and the writer, the pulleys used by Rowland would be subject to friction.

Reynolds and Moorby (1897) used, as is well known, a 70 H.P. Froude brake

* Rapports Congrès intern. d. Phys. (1900). Tome 1.

† V. Deut. phs. Ges., 10, p. 584 (1908).

‡ Dict. App. Phys., Vol. 1, p. 477.

§ For brevity J will be used for "mechanical equivalent of heat." Strictly, of course, J is the symbol for the ratio of two quantities of energy.

and continuous flow calorimeter with a temperature rise of 1.3°C. to 100°C. Steadiness of conditions is essential to such calorimetry. The speed varied, however, by as much as 3.3 per cent. in 30 minutes, and the rise of temperature by 2.7°C. in 120 seconds. An uncertain quantity of heat went to form steam bubbles in the water. The heat conducted along the steel shaft (two parts 3 in. long by 4 in. diameter) was not known with any certainty. The mean calorie in terms of which Reynolds and Moorby's result is obtained is not accurately known in terms of, say, the 20°C. cal.

Electrical Equivalent of Heat.—Griffiths' (1894) experiments are notable for the exact limitation of the boundary of the calorimeter, the determination of the heat loss, and the elimination of the heat capacity of the calorimeter. The rate of energy input (2 to 6 watt), however, is the smallest used by any observer. Schuster and Gannon (1896) determined their temperature rise of about 2.25°C. by mercury thermometers. The six experiments upon which their value of J is mainly based gave values from 4.1884 to 4.1940×10^7 . They used a filter paper coulombmeter to determine the quantity of electricity used. Callendar and Barnes (1902) used platinum thermometers, and continuous flow calorimetry, realising very steady conditions and a small heat loss. Individual experiments in a series often agreed to 1 in 10,000. W. R. and W. E. Bousfield used both the continuous flow and rise of temperature calorimetric methods with mercury in glass thermometers. An uncertain amount of heat was lost by evaporation of water from the calorimeter, and the observers had difficulties with their resistances. Jaeger and Steinwehr (1921) have made a very carefully planned investigation at the Reichsantalt. Fifty kilogrammes of water were electrically heated by a power input of 800 watts. The electrical and platinum thermometry measurements were made with every refinement for accuracy. The rise of temperatures adopted were rather small, making extremely accurate thermometry necessary.

All the electrical determinations of J , if the results are to be expressed in ergs per calorie, require to be corrected for the electrical standards used, and some of the determinations require correction for the scale of temperature. These corrections can be best explained and made explicit by writing down the correction to be made to each determination which requires correction.

It is most important, if it is possible to do so, to correct the very accurate experiments of Callendar and Barnes. Barnes in 1909* discussed the corrections to be made to their results. There are three ways of arriving at the E.M.F. of the Clark cells (denoted by e_{CB} below) used by those observers. Barnes gives reasons for believing that the E.M.F. of cells in which the mercurous sulphate has been washed with water (as it was in the older cells) is 0.28 millivolts higher than cells prepared according to recent specifications. The E.M.F. of the latter is, according to Smith,† $e_{15} = 1.4333 \cdot 10^8$ E.M.U. We have, then, $e_{\text{CB}} = (1.4333 + 0.00028) \cdot 10^8 = 1.43358 \cdot 10^8$ E.M.U.

Further, Barnes states that

$$e_{\text{CB}} = 1.40666 \cdot (\text{Weston cell at } 20^{\circ}\text{C. in 1900})$$

$$= 1.40666 \cdot (1.0188 + 0.0003) \cdot 10^8 = 1.4335 \cdot 10^8 \text{ E.M.U.,}$$

using the value given by Smith for the Weston cell, and correcting for the water

* Proc. Roy. Soc., 82, p. 390 (1909).

† Dict. App. Phys., Vol. 2, p. 271.

ashed mercurous sulphate. Callendar, however, in an appendix to Barnes' Paper, implies that King's experiments with the Clark cell give

$$e_{CB}=1.4334 \text{ . semi-absolute volts}=1.4341 \cdot 10^8 \text{ E.M.U.}$$

I have assumed $e_{CB}=1.4338 \cdot 10^8$ midway between the above values. Barnes,* assuming $e_{CB}=1.43325 \cdot 10^8$ E.M.U., and 1.01358 B.A. unit=1 true ohm (i.e., 10^9 E.M.U.) found $J=4.1783 \cdot 10^7$ erg per 20° cal. The energy input was given by an expression of the form $Ee t/R$, and so the corrected value is for Barnes

$4.1783 \cdot 10^7 \cdot (1.4338/1.43325)^2 \cdot (1/1.0005)=4.1795 \cdot 10^7$ erg per 20° C. cal. where the factor $1/1.0005$ corrects the resistance. No correction to the hydrogen scale is needed according to Professor Callendar (see below). In all the electrical determinations of J , except that of Schuster and Gannon, standards of resistance have been used based on the 106.3 cm. of mercury ohm, but it is now known that that ohm—it is the international ohm—is $1.0005_2 \cdot 10^9$ E.M.U.†

Griffiths and Schuster and Gannon used Clark cells standardised against the Cavendish laboratory cells by Glazebrook and Skinner. For these cells I assume $e_{CB}=1.4336 \cdot 10^8$ E.M.U. We get the following corrected values of J :—

$$\text{Griffiths}^\ddagger : 4.199 \cdot (1.4336/1.4342)^2 \cdot (1.0004/1.0005) \cdot (1.0011)^{-1} \cdot 10^7$$

$$=4.1904 \cdot 10^7 \text{ erg per } 20^\circ \text{C. cal.}$$

The factor 1.0004 corrects from the air to the hydrogen scale, and $(1.0011)^{-1}$ from the 15° to the 20° cal.

Schuster and Gannon§ : $4.1917 \cdot 10^7 (1.4336/1.4340) (1.00017)^{-1}=4.1898 \cdot 10^7$ erg per 20° cal. These observers used a filter paper silver voltameter, which may deposit from 1 to 10 in 10,000 more silver per absolute coulomb than they assumed.

W. R. and W. E. Bousfield|| : $4.1755 \cdot 10^7 (1.0188/1.0184)^2 \cdot (1.0005)^{-1}=4.1767 \cdot 10^7$ erg per 20° cal.

Jaeger and Steinwehr¶ : $4.1800 \cdot 10^7 (1.0188/1.0183)^2 \cdot (1.0005)^{-1}=4.1821 \cdot 10^7$ the E.M.F. of the Weston cell at $20^\circ \text{C.}=1.0183$ international volt= $1.0188 \cdot 10^8$ E.M.U. The Bousfields assumed 1.0184 int. volt.

The value given for Rowland in the following table is based on Day's correction of his results to the hydrogen temperature scale ($4.181 \cdot 10^7$ at 20°C. and 4.188 at 15°C.), and corrected for his temperature range, assuming $15^\circ \text{ cal.}/20^\circ \text{ cal.}=1.0011$. Reynolds and Moorby's results, $J=4.1832 \cdot 10^7$ erg per mean cal., is in terms of the calorie from 3° to 100°C. Dr. Ezer Griffiths and Mr. Awbery kindly inform me that 1 mean cal. = 1.002_2 cal. at 20°C. , according to data which they have prepared for the International Critical Tables. According to Professor Callendar, the ratio is 1.0016. I use 1.002.

* Phil. Trans., p. 261 and p. 172, A 199 (1902).

† Smith, loc. cit., p. 247.

‡ Griffiths, Phil. Trans., p. 314, A 186 (1895); in this author's 1894 Paper different values are given.

§ Phil. Trans., p. 458, 186 (1896).

|| Phil. Trans., p. 236, A 211 (1911).

¶ A. d. P., p. 365, 64 (1921).

Reynolds and Moorby*: $J = 4.1832 \cdot 10^7 \cdot (1.0002/1.002) = 4.1758 \cdot 10^7$ erg per 20° cal.

The value of the mean calorie is, however, somewhat uncertain, as the determinations of the specific heat of water from about 50° to 100° are discordant for data of this kind.

Mechanical Equivalent of Heat.
(Hydrogen temperature scale.)

	Erg per 20°C. cal.	Wgt.
Direct determinations—		
Rowland	$4.1822 \cdot 10^7$	2
Reynolds and Moorby	$4.1758 \cdot 10^7$	1
Indirect electrical determinations—		
Griffiths	$4.1904 \cdot 10^7$	1
Schuster and Gannon	$4.1898 \cdot 10^7$	1
Callendar and Barnes	$4.1795 \cdot 10^7$	2
Bousfields	$4.1767 \cdot 10^7$	1
Jaeger and Steinwehr	$4.1821 \cdot 10^7$	2
Weighted mean	$4.182 \cdot 10^7$	

Miculescu and Rispaill have also made determinations. The corrected results are entered in the table above, and a weighted mean value derived. The agreement between the different values entered is not very close.

The Mean Calorie.—The value of J entered against Reynolds and Moorby is evidently low. Is the error in their experiments, or is it in the value of the ratio mean cal./ 20°C. cal. used to convert their result to the 20° cal.? The question is an important one, as the mean calorie is the most convenient heat unit for expressing the thermal properties of steam, and it is desirable that its value in terms of the erg should be known. Possibly the most accurate way of finding the ratio mean cal./erg is from the ratios mean cal./latent heat of steam and erg/latent heat of steam. Carlton Sutton,† using the Joly steam calorimeter, found the latent heat of steam equal to 538.88 mean cal.

DISCUSSION.

Mr. F. E. SMITH said that he had little faith in the values of physical constants obtained by applying corrections long after the date of the observations. The Clark cell used in one instance had come into his hands, and was found to have an E.M.F. less than 0.1 volt; no one could say what its original E.M.F. was. He would be inclined to attach more weight to electrical than to mechanical determinations of J .

Mr. T. C. SUTTON: Among points of interest too numerous to mention in the time at our disposal, Prof. Laby refers to the use of the latent heat of steam as a means of determining the mechanical equivalent of the mean calorie. My own experience (Proc. Roy. Soc., A93, p.155, 1917) with various forms of steam calorimeter has convinced me that it can be developed into an instrument of great accuracy. In investigations such as we are now considering it presents many advantages, not the least of which is the fact that all thermometers can be dispensed with. The value obtained in this way for the latent heat of steam is 538.9 mean calories. In his work on the total heat of steam, Callendar derived (from electrical measurements) the value 540.2 twenty-degree calories. Consequently, if the two values were to agree, the ratio of the mean calorie to the twenty degree calorie had to be 1.002 , *f*. The accepted value at the time was 1.001 , which represented a discrepancy too great to be attributed to any obvious experimental error. I had not

* Phil. Trans., 190 (1897).

† Proc. Roy. Soc., p. 155, A 93 (1917).

the courage, at the time, to blame the accepted value of the mean calorie. It is therefore with surprise, and much satisfaction, that I now learn that Dr Griffiths and Mr. Awbery obtain the value 1.002,2, and are using this as the official figure of the International Tables. This gratifying conciliation, after a lapse of ten years, emphasises the reliability of steam calorimetry, and places the value of the latent heat of steam at the experimentally determined figure 538.9 mean calories. At the outbreak of war in 1914 I had in mind also a determination of the latent heat of steam in (a) electrical units and (b) mechanical units (methods indicated by lantern slides), and regret that at the moment I see no prospect of myself carrying these investigations to their logical conclusion.

Mr. J. H. AWBERY: The ratio between the mean calorie and the 20° calorie which I quoted Professor Laby was deduced from a consideration of all the published determinations. It is higher than the number commonly accepted previously, chiefly because of the figures of Jaeger and Steinwehr (Sitz. d. Berl. Akad., p. 424, 1915). I should like to emphasise that the agreement of the different investigations is such that no reliance should be placed on the fifth significant (fourth decimal) figure in this ratio.

Dr. EZER GRIFFITHS: Prof. Laby's Paper revives interest in a subject which occupied the attention of many physicists a quarter of a century or so ago. One cannot but admire the courage of an investigator who sets out to determine a thermal constant to an accuracy of one part in five thousand, for it will probably be as difficult to do so as to determine an electrical unit to one part in fifty thousand. Before commenting on Prof. Laby's apparatus, I would like to make a few remarks on the Paper. I view with certain misgivings attempts to correct old work unless made by the investigators themselves, as they alone are acquainted with all the facts concerning their apparatus. In the present instance many of the investigators whose work had been corrected by Prof. Laby are still living, so they can make their views known before Prof. Laby writes his final account. In the publication of work of high precision some authorities advocate the insertion of the data in great detail, so as to facilitate subsequent correction. The plan I would like to suggest is that the investigator should take steps to preserve his apparatus, so that the experiments can be repeated with such modifications as experience dictates. It will, I think, be generally admitted that the development of the method and the technique absorbs most of the time in an investigation, so a repetition would not be a formidable undertaking. When our President designed the Lorenz apparatus for the determination of the ohm, he so arranged matters that all the essential measurements could be checked at any time. If anyone in future were dissatisfied with the value ascribed to the ohm, he could re-determine it, basing his measurements solely on his own metre rule and clock and using this apparatus. As regards methods for the determination of J , the simplest to operate at the present time is the electrical. The electrical units are now known to an accuracy of at least one part in 10,000; it is improbable that a calorimetric determination can be made to one part in 5,000, one of the reasons being that we do not know of a heat insulator comparable with a first class electrical insulator, such as amber. I would further advocate working on a large scale, so that corrections for heat capacity of the container, stirrer, etc., would be relatively very small. I consider that the weight attached by physicists to Reynolds and Moorby's result is an unconscious tribute to large scale experiments, and I am surprised that no one has repeated the test using standard thermometers to measure the temperature rise over a narrow range, instead of between 0° and 100°C. The objections raised by Prof. Laby to Reynolds and Moorby's experiments could be overcome with modern engineering appliances.

Mr. G. M. CLARK: In re-introducing myself to the meetings of the Society after an absence of more than 25 years spent abroad, I may say that it was my pleasure and honour to be associated with Griffiths from 1887 to 1892 during the period of making the determination of J , and I warmly welcome the proposal of the author to revise the value of this constant. I doubt whether much is gained by discussing the results of other observers by making known corrections that arise through the light of later knowledge. Every physical determination is a shot at a target, and by the removal of certain errors it is by no means certain that the remainder give a better probable value for the centre of the target. The tables put forward by the author are, however, not only of use for the point that the author wished to make—namely, the necessity for revision—but they are also of use as showing that the halo of nebulousity surrounding any physical determination is probably greater than the original experimenter cared to acknowledge to himself. I am also of opinion that the only person who can revise any old determination is the person who made it. One of the obscure causes of uncertainty about which very little is said is the formation

of steam bubbles or any evaporation that takes place from the calorimeter either in steady flow or other form. When it is remembered that it takes about 500 calories to evaporate water and only 1 calorie to heat it up a degree, it is evident that very little evaporation, which might take place in the body of the water to be heated, would produce an error in the direction of reducing the final value. It is, therefore, almost essential to use a different method as Griffiths has done, heating first by stirring alone and then with increasing current, and calculating from the difference the work done. It is rather a matter of luck whether this eliminates the obscure uncertainties that are bound to occur in all calorimetry. I admire very much the author's apparatus and equipment and contrast it with our own of nearly forty years ago, when storage batteries were unknown and part of our time for experimental work was taken up with fitting up Bunsen's cell with strong nitric and sulphuric acids. It was impossible at that time to get small electric motors for driving stirrers, etc., and even the laboratory was not lighted with electric light. Over two years of our time were spent in research into thermometry, which was a side show to the main determination, but involved such work as the development of the platinum resistance thermometer, and the fixing of its standardisation point, the boiling point of sulphur. I envied the author his being able to start up with so much modern equipment, and though the difficulty of measurement increases by about the fifth power of the accuracy, I hope that this modern equipment will remove about three of them and not more than the square would be left for the author to contend with. I wish him every success in his work, and feel that he can do it whole-heartedly as one who has already been thoroughly over the ground in every detail.

Prof. E. H. GRIFFITHS (communicated): I regard a critical discussion, such as given by Prof. Laby, as of high value. Had I time I should have wished to comment on his methods of reduction and the conclusions he arrives at. I will, however, only refer to his remarks upon my own determinations. In line 18 on page 171 he states, "Griffiths: 4.199." In Dict. App. Physics Vol. I., p. 493, Table X., I give what I consider as the final value resulting from my own experiments—viz., 4.184 cal. at 20°C. of the hydrogen scale. Curiously enough, this is identical with the "weighted mean" arrived at by Prof. Laby. In this 1924 article I have given my reasons for each step in the reductions. I confess that it appears to me that it is the final, and not the earlier, conclusions of an author which should be quoted.

Prof. H. L. CALLENDAR (communicated): The "Continuous Electric Method" of calorimetry was designed with the primary object of determining the variation of the specific heats of water and mercury over the range 0°C. to 100°C., for which it appeared to be the most suitable method available. Careful attention was paid to the details of platinum thermometry and temperature regulation, and the *constancy* of the standard cells and resistances employed was verified with the utmost precision. The results for the variation of the specific heat of water were subsequently confirmed by an independent method, called the "Continuous Mixture Method" (Phil. Trans. A, 212, p. 1, 1912). The several formulae previously employed were combined into a single equivalent formula possessing special advantages, which gives the following values for the ratio of the mean calorie and the 15° cal. to the 20° calorie; mean calorie 1.0016, 15° calorie 1.0012 respectively. Reynolds' value for the mean calorie corrected for the range 0°C. to 100°C. becomes 4.1837 joules per cal. in place of 4.1832 for the range 1.3°C. to 100°C., and corresponds to a value 4.1770 for the 20° calorie. The value 4.1932 given by Prof. Laby is probably an accidental error.

The most unsatisfactory point in the reduction of Rowland's observations to the hydrogen scale is that the thermometers could not be compared with the gas thermometer under the actual conditions of the experiment on a rapidly rising temperature. This is one of the reasons why it is necessary to employ platinum thermometers directly in experiments of this nature. The zero lag of a mercury thermometer on a changing temperature tends to give results which are too small for the temperature interval, or too large for the value of J . The correction from the nitrogen to the hydrogen scale was taken as +3 parts in 10,000 from Chappuis' corrected results (Phil. Trans. A, 199, p. 101, 1902). It was found that this correction was compensated throughout the range 0°C to 100°C. by a small correction of opposite sign due to variation of the temperature gradient in the flow-tube. Both corrections were omitted by Barnes in his final table, which, therefore remains correct (loc. cit., p. 129) as if they had both been included.

In the reduction of the results to absolute units (joules per gm. cal.) at any temperature, the conventional value 1.4342 int. volts was assumed for the Clark cells, and the international ohm was taken as being equal to the absolute ohm. The result obtained in this way is given as 4.1837 joules per gm. cal. at 20°C. in Barnes' table 1902. The experiments of Ayrtton and Mather with the Lorenz apparatus, destined for McGill College, and those of King with the electro-dynamometer

in 1897, had already shown that this result was too high, but the absolute values of the electrical units required further investigation. Barnes' ratio 1.40666 of the Clark cell to the Weston cell has since been confirmed, and the cells set up with washed mercurous sulphate in 1900 exceed the modern cells by 0.30 millivolt. Adopting these data, we agree with Prof. Laby in finding 1.4335 abs. volts for the old Clark cell in place of the assumed value 1.4342. If we also take the international ohm as being 1.0005 absolute ohm, Barnes' original results require to be reduced by nearly 10 in 10,000 for the cells, and by 5 in 10,000 for the ohm, giving Callendar and Barnes 4.178 joules per gm. cal. at 20°C. I have generally taken the value 4.189, giving greater weight to Rowlands' direct determination.

Mr. W. R. BOUSFIELD (communicated): With reference to the determination by W. R. and W. E. Bousfield, it is said that the "observers had difficulties with their resistance." This idea must have arisen from the fact that we investigated the difficulties with a wire resistance for heating, and abandoned it, and used instead the new device of a "mercury thermometer resistance." This was shown to be extraordinarily accurate, and was used throughout with excellent results. It is also stated that "an uncertain amount of heat was lost by evaporation of water." This was only the case with high temperatures. From 0° to 40° this heat loss was determined with great accuracy.

The comparative figures for our determinations and those of Callendar and Barnes do not appear to be correctly stated in Prof. Laby's Paper. Our results (*see* p. 241 of our Paper) from 13° to 55° mean value were—

$$J = 4.182.$$

Callendar and Barnes for the same interval were—

$$J = 4.175.$$

Yet Prof. Laby seems almost exactly to *reverse* these figures. I do not know what sort of corrections can have been applied to produce these figures. Our results were subsequently confirmed by an independent investigation.* The question of wire resistances was taken up in a subsequent Paper in the Proc. Roy. Soc. by Glazebrook, Bousfield and F. E. Smith, the reference to which I have not at hand.

AUTHOR'S reply: I think that some of the electrical standards used in the J experiments of the past can be expressed in electro-magnetic units. No doubt the values of the older standards of E.M.F. are quite uncertain, but the E.M.F. of the Weston cells used by the Bousfields and by Jaeger and Steinwehr is known, and so is the value of the standards of resistance used even in 1892. The ohm appears to have been pretty accurately 106.3 cm. of mercury, or 1.0005×10^9 E.M.U. for over twenty years. I agree with practically all that Prof. Callendar says, and I have accordingly made certain changes in the Paper above. In correcting our own experiments to 20°C., Mr. Hercus and I have used for some years Prof. Callendar's 1912 formula for the variation of the specific heat of water with temperature, as being the most accurate available. In view of his statement that Barnes' results are in effect already corrected to the hydrogen scale I now omit that correction. That his results are effectively on that scale is not, I think, mentioned in Barnes' Paper, and I overlooked that it is mentioned in Prof. Callendar's.

Dr. E. H. Griffiths' results are very valuable for the reasons stated in the text, but the E.M.F. of the Clark cell which he used is uncertain.

With reference to several criticisms, it is necessary to stress that on the pages quoted in the footnotes to my Paper will be found the authority for the data which have been used in it.

* See Bousfield, Specific Heat of Water, Proc. Roy. Soc., A, 93, p. 588 (1917).

XXI.—THE PRESENT STATUS OF THEORY AND EXPERIMENT RELATING TO SPECIFIC HEATS AND THE CHEMICAL CONSTANT.

By F. IAN G. RAWLINS, Trinity College, Cambridge.

Received October 5, 1925.

(Communicated by Dr. D. OWEN.)

ABSTRACT.

The theoretical and experimental aspects of the specific heats of solids, liquids and gases in the light of present knowledge are discussed. Possible lines of advance have been indicated for solids in view of the progress now being made in X-ray crystallography, and the importance of further experimental work on compressibilities and elastic constants is suggested. Tentative views on the specific heat of liquids are given. In gases the quantum theory of rotational heat is shown to fail to account satisfactorily for the behaviour of hydrogen at low temperatures. The chemical constant of monatomic and diatomic substances is discussed, both from a thermodynamic and from a statistical point of view. Current views on the nature of this constant are described. The theory of gaseous degeneracy and its bearing upon specific heats and chemical constants is reviewed.

IN this paper an attempt will be made to convey some idea of our present knowledge, both theoretical and experimental, of the specific heats of solids, liquids and gases. This theme can perhaps most profitably be treated by including a discussion of the chemical constant, both in its statistical aspect and also in regard to its function as a constant of integration in the vapour-pressure equation. Recent work has brought to light some interesting discrepancies between the value of the chemical constant thus found and that deduced from dissociation equilibria. Attention will also be directed to the subject of Gaseous Degeneration, to which Eucken, Mache and Bennewitz have given much attention of late years, and which affords an opportunity of studying the theory of specific heats and chemical constants in close relationship.

For clarity of treatment the following scheme suggests itself :

- (1) *Specific Heats.*
 - (a) Solids.
 - (b) Liquids.
 - (c) Gases.
- (2) *Chemical Constants.*
 - (a) Monatomic substances.
 - (b) Diatomic substances.
- (3) *Gaseous Degeneration.*

Both with particular reference to specific heats, also to chemical constants.

- (4) *Summary.*

With regard to the particular weight attached to theory and experiment, the aim is to describe experimental results where they confirm or fail to bear out the theory. Except in one instance (in the section on the specific heats of liquids), actual laboratory arrangements are not described. The special calorimetric apparatus

Devised by Nernst for work on the specific heat of solids is hardly novel enough to need detailed attention here.

(1) SPECIFIC HEATS.

a) Solids.

Excluding the early work of Einstein and the semi-empirical attempts of Nernst and his pupils, the first theory of the specific heats of solids embodying a quantum partition of energy was due to Debye. His conception, however, includes the classical view of elasticity, leaving out of consideration the atomic nature of the substance. In fact, it treats solid bodies as structureless continua. In reality, assuming that the body consists of N atoms, there cannot be more than $3N$ natural frequencies. Debye obtains the upper limit of the elastic spectrum ν_{\max} by stopping arbitrarily at the $3N$ th natural period. It is interesting to inquire how the value of ν_{\max} formed from the elastic constants compares with the value of ν_{\max} as deduced from specific heat measurements, using Debye's formula.

A table given by Eucken on page 102 of his "Grundriss der physikalischen Chemie" shows that ν_{\max} (elasticity) is generally some 5 per cent. higher than ν_{\max} (thermal). It is only by stressing the weakest part of Debye's theory—i.e., that the vibrations in a solid fall off suddenly at a perfectly defined frequency, ν_{\max} —that agreement could be expected. The agreement between ν_{\max} (thermal) and the frequency deduced by Lindemann's formula is erratic, as might be foreseen from the consideration that it is only at the melting point temperature itself that it has any very definite physical basis.

The difference, however, is as little as 3 per cent. between ν_{\max} (thermal) and ν (Lindemann) for monatomic elements of low melting point, whereas for the diamond it amounts to some 15 per cent.

Generally speaking, Debye's theory is fairly well confirmed by experiment for monatomic substances, as well as the corollary that at very low temperatures the molecular heats of all solids (not necessarily monatomic) should be proportional to the third power of the absolute temperature. Debye's equation demands that the molecular heats of solids should vanish at the absolute zero, approaching the classical value $3R$ when T/θ is greater than 0.9 (T is the absolute, θ the "characteristic temperature," which for the majority of substances lies between 100 and 200). Several attempts have been made to extend Debye's theory to solids other than chemical elements. The conception of a solid as a mass of similar atoms now gives place to that of a collection of similar molecules. Within each molecule exist vibrations of a type which will be considered later in connection with the specific heat of gases. For a solid consisting of N molecules, if we sum the contributions from the vibrations within the molecules and the motions of the molecules themselves, an expression of the form

$$E = 9N \int_0^{\nu_{\max}} \frac{h\nu^3}{e^{\frac{h\nu}{KT}} - 1} \cdot \frac{d\nu}{\nu_{\max}^3} + N \sum \frac{h\nu_1}{e^{\frac{h\nu_1}{KT}} - 1} \dots \dots \dots (1)$$

results for the energy. The summation is to be extended over all the internal molecular vibrations. For a diatomic substance the summation reduces to a single "Einstein" term. In confirmation of this formula, Nernst* shows if by ν_1 is understood the frequency of a Rubens absorption band in the infra-red, very fair

* Vorträge über die kinetische Theorie der Materie, p. 81 (1914).

agreement is obtained with the experimentally-determined values of the specific heats of simple compounds. The conception involved in (1) is, however, very crude. Clearly, interaction of a very complicated kind takes place between the whole assembly of atoms within the solid, so that it is not justifiable except as the roughest of approximations to regard the vibrations as being capable of being split up into those within the molecule and those in which the molecule as a whole is concerned. It is easy to see that if all the atoms in a solid are taken to be alike, (1) does not reduce to the simple Debye expression for the energy of an element. Schaefer has recently shown* that Debye's T^3 law cannot be valid at extremely low temperatures; in such a region an exponential law is demanded.

Better results are likely to be obtained by the use of the Born and Karman theory,† which takes account of the crystal lattice. Since from the work of W. H. and W. L. Bragg and others the type of lattice is known with certainty for a large number of crystals (both elements and compounds), it may be expected that considerable progress will occur along these lines. A particularly interesting point is the question of the molecular lattice, which is of some consequence in one of the writer's papers. From evidence which is given there it appears that the crystal structure of the halogen hydrides is very different from that of binary salts, such as NaCl. The suggestion is that the unit is not the atom (or ion), but the molecule. A recent paper‡ has given some grounds for thinking that the same is true for the halogens.

For iodine, however, a single frequency $\beta\nu=106$ represents the specific heat admirably, from which it might be inferred that iodine is atomic in the solid state (as opposed to a molecular grouping). The two allotropic forms of zinc sulphide, zincblende and wurtzite might prove of interest in this way. The lattice of ordinary zincblende is certainly atomic (Eucken's "Grundriss," p. 480), but in wurtzite the structure is molecular (Eucken, loc. cit.). The specific heat of zincblende can be fitted excellently to a Debye function with $\beta\nu=175$. An experimental determination of the specific heat of wurtzite, especially at low temperature, might prove illuminating. One would expect that, in view of its molecular structure, it would deviate considerably from Debye's curve.

Measurements of specific heats usually refer to C_p (the specific heat at constant pressure), whereas for a comparison with theory C_v (the specific heat at constant volume) is required. For metals, the usual method of obtaining C_v is by means of the equation

$$C_p - C_v = \frac{wa^2eT}{\rho} \dots \dots \dots (2)$$

where w is the atomic weight, a the coefficient of cubical expansion, e the volume elasticity and ρ the density. When we come to crystalline salts the lack of data necessary for (2) makes it imperative to seek a different method. Nernst and Lindemann§ obtain a formula

$$C_p - C_v = C_p^2 TA \dots \dots \dots (3)$$

where A is a constant characteristic of the substance which may be deduced from measurements of the compressibility and coefficient of expansion made at one tem-

* Zeit. für Physik, 7, p. 287, (1921).

† Born, Der Dynamik der Kristallgitter, 2nd edition.

‡ Friederich, Zeit. für Phys., 31, p. 813 (1925).

§ La Théorie du rayonnement et les quanta, p. 265 (1912).

perature. Really, equation (3) rests upon Grüneisen's observation that the coefficient of expansion is proportional to the atomic heat. According to Eucken ("Gründriss," p. 485), the compressibility k of a crystal is related to the grating constant d by the simple equation

$$K = 5.68 \times 10^{18} \cdot d^4 \quad (4)$$

The agreement with observation is very good, as the following examples show. They are typical of a fair number of results.

					$K_{\text{obs.}}$	$K_{\text{from (4)}}$
NaCl	4.1×10^{12}	3.56×10^{12}
KI	8.6×10^{12}	8.68×10^{12}
TlCl	4.7×10^{12}	4.69×10^{12}

The importance of this is for the evaluation of the constant A in equation (3) if, as is often the case, the crystal structure is known.

Naturally, it is hardly possible to use (4) for crystals possessing a molecular lattice.

In considering the molecular heats of solids as a function of the temperature, great care is needed to make sure that any allotropic changes are observed and their heats of transformation recorded. Thus, there are three forms of solid oxygen, two of solid nitrogen, two of carbon monoxide, two at least of iodine (the transition being extremely slow). In connection with the deduction of the chemical constant from thermodynamical equations, these transformations are of considerable importance.

It remains now to discuss the specific heat of solids at high temperatures.

The fact is that in the neighbourhood of $1,000^\circ\text{C}$. the atomic heat at constant volume of certain solids has been found to exceed the classical value $3R$ very considerably. There must therefore be some source of internal energy to be taken into account in addition to the atomic vibrations. Presumably, this is due to the movements of electrons within the atom. This electronic energy is negligible at low temperatures compared with that possessed by the atoms, but by no means so at high temperatures where it will make itself felt in the atomic heat.

Koenigsberger* has attacked this problem, and considers that C_v should reach the value 9 (instead of 5.95) if the vibrations of the electrons are taken into account. The following are examples:—

Metal.					Temp.-Range.	C_v
Ag	900°C .	6.7
Cu	900°C .	7.1
Al	650°C .	7.7
Ni	$1,150^\circ\text{C}$.	7.9
Sn	$1,100^\circ\text{C}$.	9.2
Fe	$1,200^\circ\text{C}$.	9.6

(b) Liquids.

A satisfactory discussion of the specific heats of liquids is difficult, in that there is at present no guiding principle possessing physical significance. In this section reference will be made to the suggestions of Honda,† as being the only attempt—

* Zeit. für Electrochem., 17, p. 289 (1911)

† Phil. Mag., 45, p. 189 (1923).

as far as the writer is aware—to give a tentative theory of the subject. Before going into this, it may be convenient to state a few general results which have been accumulated in recent years.

* In general, the specific heat of a liquid is of the same order of magnitude as that of the same substance in the solid state, though inclined to be higher. C_p usually rises considerably with the temperature, either linearly or as a curve which gets steeper with increasing temperature.

There are some interesting exceptions showing great irregularity, which

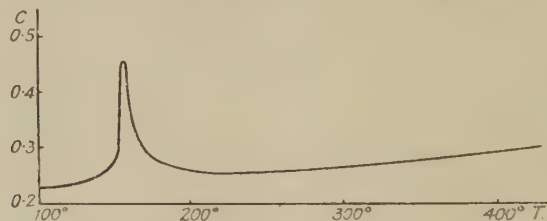


FIG. 1.—HEAT CAPACITY PER GRAM OF LIQUID SULPHUR (LEWIS).

indicates a change of molecular constitution. In liquid sulphur, for instance, there is a sharp maximum at 160°, which is clearly connected with the existence of the two molecular species S_λ and S_μ (probably S_8 and S_6).

The heat absorbed is largely devoted to increasing the amount of the latter at the expense of the former. Williams and Daniells* have recently examined a number of organic liquids in their adiabatic calorimeter. Benzene, for example, shows a number of irregularities indicative of molecular changes. The authors find that water acts as a catalyst in bringing about the transformation from one

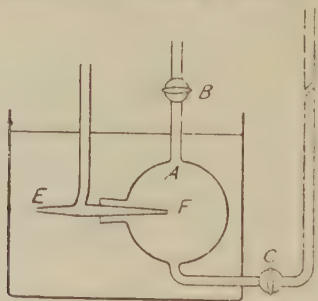


FIG. 2.—ARRANGEMENT FOR THE DETERMINATION OF THE HEAT CAPACITY OF LIQUIDS.

molecular species to another. They suggest that differential specific heat determinations would offer a good way of studying the phenomenon of association in liquids.

A method suggested many years ago for measuring the specific heats of liquids has lately been revised in a modified form by Barus.† It depends upon the thermodynamical equation

$$\left(\frac{\partial T}{\partial p}\right)_s = \frac{T}{C_p} \left(\frac{\partial v}{\partial T}\right)_p$$

* Amer. Chem. Soc. Journ., 46, p. 1569 (1924).

† Publ. Carnegie Inst., 249, 9, 4 (1919).

The flask *A* contains the liquid under investigation. It is placed in a thermostat and brought to an even temperature, recorded by a sensitive thermocouple *EF*. The cock *B* (hitherto open to maintain atmospheric pressure) is now closed and *C* opened. The quotient of the increase in temperature by the applied pressure gives $\left(\frac{\partial T}{\partial p}\right)_s$. If the coefficient of expansion $\left(\frac{\partial v}{\partial T}\right)_p$ is known, C_p follows.

Honda's theory of the specific heat of liquids may be outlined thus. It applies mainly to monatomic substances. The atoms in a solid perform vibrations according to the usual theory with the mean energy $3Rf\left(\frac{\theta}{T}\right)$, θ being the characteristic temperature. In addition to this, Honda assumes that the atoms have some kind of rotational oscillations about their centre of gravity in the solid, a constraint being imposed by the directive forces of neighbouring atoms. Fusion is supposed to take place when the energy of the rotational oscillations becomes so great that the atoms execute continuous rotations. Honda neglects the work done against cohesion, and explains the latent heat of fusion as the energy which these new degrees of freedom of continuous rotations must acquire.

Lindemann discusses these assumptions, and shows that on the whole they are untenable.

For instance, it is not difficult to see that a characteristic temperature of the order 5×10^6 would be required, which is of a totally different order from the figures usually considered. Again, a negative heat of fusion would result, as Lindemann shows. However, Honda arrives finally at the result that the difference $C_v - C_v^1$ between the atomic heats of the liquid and solid phases of the same substance is equal to $R\left(\frac{n}{2} - 3e\right)$, when n is the number of degrees of freedom of the atoms in the liquid, and e lies between 0 and 0.5.

(c) Gases.

(i) *Monatomic*.—Here there are three degrees of freedom (translational). On the classical theory, the molecular heat C_v is constant and equal to $\frac{3}{2}R$. This is in accordance with experiment up to the highest temperatures. At very low temperatures Eucken has found marked deviations from the value $2.98 \frac{\text{cals.}}{\text{degree}}$. The significance of this effect will be discussed in the Section dealing with gaseous degeneration.

(ii) *Diatomic*.—The number of degrees of freedom is now six. On the classical theory of equipartition, provided all the degrees are effective, the molecular heat of an ideal diatomic gas is independent of the temperature and equal to $\frac{7}{2}R$. This is contradicted by experiment. Eucken has found that at low temperatures hydrogen behaves as a monatomic gas with $C_v = \frac{3}{2}R$, corresponding to the translational degrees alone. Also at $2,000^\circ\text{C}$. the molecular heat is only 6.5 instead of 6.98; i.e. $\left(\frac{7}{2}R\right)$.

Generally speaking the atomic vibrations in a diatomic gas are of high frequency. ν is of the order 10^{14} , falling in the short infra-red. According to the quantum theory, the probability that the vibrations will contribute an appreciable amount to the molecular heat becomes very small, even if the temperature is not very low. The molecular rotations are of much lower frequency (of the order 10^{12}), and consequently persist at a temperature at which the vibrational term would be negligible, since the quantum $h\nu$ associated with rotation is much smaller than that associated with vibration. At any given temperature, therefore, the chance of possession of a rotational quantum is greater than that of a vibrational quantum. With decreasing temperature the probability of the possession of a quantum of any size grows less, so that at very low temperatures even $C_{\text{rot.}}$ vanishes, leaving the translational term alone.

It will be convenient to write the specific heat of a diatomic gas in the form

$$C_v = C_{\text{trans.}} + C_{\text{rot.}} + C_{\text{vib.}} \quad \dots \dots \dots (5)$$

and to consider the contributions separately. Excluding for the present the possibility of "degeneracy," $C_{\text{trans.}}$ is constant and equal to $\frac{3}{2}R$.

$C_{\text{rot.}}$ has been investigated by various workers. On the basis of the dumb-bell model, Reiche* arrives at a general expression of the form

$$C_{\text{rot.}} = R\sigma^2 \frac{f(x)}{g(x)} \quad \dots \dots \dots (6)$$

where $\sigma = h^2/8\pi^2 JKT$ (J is the moment of inertia), and $f(x)$ and $g(x)$ are series in ascending powers of x , where $x = e^{-\sigma}$. For low temperatures $\frac{C_{\text{rot.}}}{R}$ tends to zero, and at higher temperatures to unity, as demanded by the classical theory.

In order to obtain a steadily rising curve it is necessary to make certain assumptions regarding the *a priori* probabilities or weights of the different quantum states. Thus, it appears that the rotationless state $n=0$ must be suppressed (otherwise the curve rises to an intermediate maximum before reaching $C_{\text{rot.}} = R$), and, further, the best agreement with experimental points, in the case of hydrogen, is obtained when the weight n or $2n$ (indistinguishable from one another) is assigned to the n th quantum state. None of the curves computed by Reiche, or the other workers along similar lines, succeed in accounting for all the observations, especially those in the neighbourhood of 200° absolute. It must be admitted that at present this problem remains unsolved.

With respect to the contribution $C_{\text{vib.}}$, assuming that the atomic vibrations can be taken as independent of the molecular rotations, this can be represented by a "Planck" term as for a simple oscillator

$$C_{\text{vib.}} = R \left(\frac{h\nu_0}{KT} \right)^2 \frac{e^{-\frac{h\nu_0}{KT}}}{\left(1 - e^{-\frac{h\nu_0}{KT}} \right)^2} \quad \dots \dots \dots (7)$$

This is analogous to the expression used in the theory of the specific heat of solids.

* Ann. der Phys., 58, p. 657 (1919).

except that there the number of degrees of freedom is three, whereas here it is one. The frequency ν_0 should correspond to the difference between the centres of successive bands in one family in the band-spectrum of the gas.

This "Planck" term becomes of some importance in the deduction of the chemical constant, as Cox* has shown in his work on iodine and bromine.

The expression for C_v thus becomes

$$C_v = \frac{3}{2}R + \sigma^2 R \frac{f(x)}{g(x)} + R \left(\frac{h\nu_0}{KT} \right)^2 \frac{e^{-\frac{h\nu_0}{KT}}}{\left(1 - e^{-\frac{h\nu_0}{KT}} \right)^2} \dots \dots \dots (8)$$

For large values of T , the second and third terms tend to R (giving C_v the classical value $\frac{7}{2}R$), and for small values of T to zero ($C_v = \frac{3}{2}R$). As examples of experimental results the following may be quoted :

					approx.
For chlorine at 1,200°C.	$C_v = 7.0$
For nitrogen at 2,000°C.	$C_v = 6.7$
For oxygen at 2,000°C.	$C_v = 6.7$
For hydrogen at 2,000°C.	$C_v = 6.5$

Chlorine thus shows very nearly the theoretical value 6.98.

Some examples of low-temperature observations are given in the section on gaseous degeneracy.

(iii) *Polyatomic*.—Both theory and experiment are considerably less developed here. Some interesting work has, however, been done by Urey† on the rotational heat of methane. He uses exactly the same method as Reiche, but sets all three moments of inertia equal to one another ($J = 2.232 \times 10^{-41}$ grs. cms.²). In the usual way

$$\frac{C_{\text{rot}}}{R} = R\sigma^2 \frac{d^2}{d\sigma^2} \log Q$$

where $Q = \sum_1^{\infty} n^2 e^{-\sigma n^2}$.

A sketch of Urey's curve is given. Bjerrum, in 1914, contributed a large amount of work on the molecular heats of CO_2 , NH_3 and water vapour. No theory corresponding to that existing for diatomic gases has yet been formed. In general, C_v depends more markedly upon temperature for polyatomic gases, but this dependence is very imperfectly known. Before concluding this account of the specific heat of gases two subjects claim brief attention : the effect of pressure upon specific heat and the specific heat of a dissociating gas.

Partington and Shilling, in their book "The Specific Heat of Gases" (Benn, 1924), starting from the usual thermodynamical equation $\left(\frac{\partial C_p}{\partial p} \right)_T = -T \left(\frac{\partial^2 V}{\partial T^2} \right)_p$, assume Van de Waal's equation of state, and show that $C_p = ap + b$, so that the relation is

* Proc. Camb. Phil. Soc., 21, p. 541 (1923).

† Jour. Amer. Chem. Soc., 45, p. 1445 (1923).

linear, which bears out the results of Lussana and Joly. Modern work has not confirmed this. For an ideal gas, $\left(\frac{\partial V}{\partial T}\right)_p$ is constant, so that C_p is independent of the pressure.

In the process of dissociation of a gas which has split up completely or partially into two or more elementary gases, the heat equivalent of the work of dissociation makes a considerable effect upon the apparent specific heat.

Consider the undissociated gas at pressure p . The heat absorbed per molecule for a rise of temperature dT is $C_p dT$.

This quantity $C_p dT$ consists of four parts :

A. The quantity of heat needed to raise the undissociated portion through

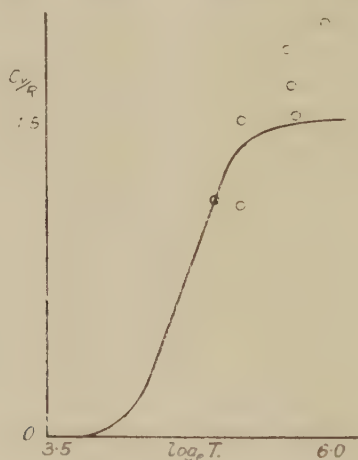


FIG. 3.—THE ROTATIONAL HEAT OF METHANE (UREY).

dT at constant volume. This amounts to $(1-a)C_v dT$ if a is the degree of dissociation and C_v is the molecular heat of the undissociated gas.

B. The quantity of heat required to raise the products of dissociation through the same temperature interval. This will be equal to

$$(n_1 C_{v1} + n_2 C_{v2} \dots + n_s C_{vs}) a dT,$$

where $n_1 \dots n_s$ are the number of mols. of each gas for one mol. of the original gas.

C. The heat equivalent of the work of dissociation $p \left(\frac{\partial V}{\partial T}\right)_p$, where V is the volume of the original gas plus that of the products of dissociation.

D. The heat of dissociation (absorbed) $= Q_0 \left(\frac{\partial a}{\partial T}\right)_p dT$, assuming that Q_0 is constant.

Thus the total is

$$C_p = (1-a)C_v + a(n_1C_{v1} + n_2C_{v2} \dots + n_sC_{vs}) + p \left(\frac{\partial V}{\partial T} \right)_p + Q_0 \left(\frac{\partial a}{\partial T} \right)_p \dots \quad (9)$$

Swart tested this equation for the process $N_2O_4 \rightleftharpoons NO_2 + NO_2$, and found satisfactory agreement.

(2) CHEMICAL CONSTANTS.

(a) Monatomic Substances.

The thermodynamic vapour-pressure equation for a solid element with monatomic vapour may be written

$$\log p = -\frac{\lambda_0}{RT} + \frac{C_{p.g}}{R} \log T - \int_0^T \frac{dT}{R T^2} \int_0^T C_k dT + i \dots \dots \dots (10)$$

where λ_0 is the heat of vapourization at the absolute zero, $C_{p.g}$ is the molecular heat of the vapour at constant pressure, C_k that of the solid. i is a constant of integration, now generally known as the chemical constant. From statistical considerations, Stern* and Tetrode obtain the expression

$$i = \log \frac{(2\pi m)^{3/2} K^{5/2}}{h^3} \dots \dots \dots (11)$$

in the usual notation, which can be put in the simple form

$$\begin{aligned} i &= -i_0 + \frac{3}{2} \log M \\ &= -1.589 + \frac{3}{2} \log M \dots \dots \dots (12) \end{aligned}$$

(M is the molecular weight), taking $h = 6.55 \times 10^{-27}$, $N = 6.06 \times 10^{23}$, $K = 1.372 \times 10^{-16}$. The agreement between the values of i from (10) and (12) is found to be satisfactory for a variety of substances. Egerton† has recently collected together a considerable amount of evidence depending only upon vapour-pressure and specific heat measurements (except in two cases) in favour of the value 1.589 for the constant i_0 . He makes no mention of two outstanding exceptions to the Stern-Tetrode formula (11).

Ladenberg and Minkowski‡ have found a discrepancy outside the limit of experimental error for sodium and potassium. From the observed value of i , equation (12) furnishes $i_0 = 1.30$ (from Na) and $i_0 = 1.37$ (from K), instead of 1.589 as theory demands. Schottky§ has questioned whether the quantum weight of the solid is necessarily the same as that of the vapour. This seems to be true for the majority of substances, whereas for sodium and potassium it may be greater for the vapour than for the solid. Another instance of this is monatomic iodine. The simple formula (12) is only true if the weights in the two states are the same. On the other hand, Eucken|| writes: "It is not inconceivable that sodium and potas-

* Phys. Zeit., 14, p. 629 (1913). Zeit. für Electrochem., 25, p. 66 (1919).

† Proc. Phys. Soc., 37, p. 75 (1925).

‡ Zeit. für Phys., 8, p. 137 (1921).

§ Phys. Zeit., 22, p. 1 (1921); 23, p. 9 (1922).

|| Ergebnisse der exakten Naturwissenschaften, I, p. 146 (1922).

sium, in the particular temperature interval in which the vapour-pressure curve has been most accurately established, may be partly associated into molecules, whereas the chemical constant has been deduced from the vapour-pressure equation for monatomic substances. The appearance of a band-spectrum in pure potassium vapour indicates the presence of molecules, since band-spectra, according to our present knowledge, are only given out by molecules, not by atoms."

An interesting general point may conveniently be discussed here. Is the chemical constant a special property of the gaseous or of the condensed state? From purely thermodynamical considerations it is difficult to give a satisfactory answer, because we are only dealing with the difference of certain magnitudes, not their absolute values. For instance, the maximum work is a measure of the change of free energy, and in the same way the chemical constant, as it appears in the vapour-pressure equation, is only a measure of the difference between a certain quantity belonging to the solid (or liquid) state, and the corresponding quantity in the gaseous state. It is possible to go a stage further if we take Nernst's Theorem into count in its application to chemical reactions. The chemical constant i here appears in the integrated expression for K_p (the dissociation constant), and, since no condensed phase is supposed to be present, it is reasonable to associate i with the gaseous state. Perhaps the most effective argument is that i (in the vapour-pressure equation) for two allotropic forms of a solid is found to be the same. Although the constitution of the two modifications is different, yet the vapour is the same for both of them. From this it may well be inferred that i is a quantity characteristic of gases.

The opposite point of view has at least one important consideration to recommend it. Equation (11) contains Planck's constant h , which can only be explained on a quantum-theory partition of energy. So far we have only considered the application of such principles to vibrations and rotations, not to translational motion, of which the whole energy in monatomic gases is supposed to consist. From this aspect the tendency would be to ascribe the chemical constant to the condensed state.

(b) *Diatomic Substances.*

We have now to consider the two equations:

For the dissociation $X_2 \rightleftharpoons 2X$

$$\log K_p = -\frac{Q_0}{4.571T} + 1.5 \log T - \frac{1}{4.571} \int_0^T \frac{dT}{T^2} \int_0^T C_{vib.} dT + 2i_x - i_{x_2} \quad \dots \quad (13)$$

where Q_0 is the heat of dissociation at absolute zero.

For the vapour-pressure

$$\log p = -\frac{\lambda_0}{4.571T} + 3.5 \log T - \frac{1}{4.571} \int_0^T \frac{dT}{T^2} \int_0^T [C_{vib.} - C_k] dT + i \quad \dots \quad (14)$$

whilst the statistical work of Ehrenfest and Trkal* leads to the formula

$$i = \log \frac{(2\pi m)^{3/2} \cdot 8\pi^2 J \cdot K^{7/2}}{\sigma h^5} \quad \dots \quad (15)$$

* Proc. Amst. Acad., 23, p. 162.

Comparing this with the result for monatomic substances (equation (11)), i (diatomic) is now seen to be a function of the moment of inertia J of the molecule, and a quantity $\frac{1}{2}$, the symmetry number. For the validity of (15) it is necessary that the rotations be fully excited. i as thus defined is the same as Langen's* "chemical constant in the normal state."

The moment of inertia is now known with considerable accuracy from band-spectrum data for a number of diatomic gases, as well as the triatomic molecules CO_2 and H_2O . For triatomic gases J in the formula is replaced by $\sqrt{J_1 J_2 J_3}$, where J_1, J_2, J_3 are the principal moments of inertia. At present a certain amount of discord exists between the values of i (diatomic), as formed thermodynamically, and those calculated on the statistical basis.

In several instances this may be due to the uncertainty which exists in connection with the factor σ . Ehrenfest and Trkal introduce this magnitude into their statistical calculations to allow for the fact that in a symmetrical molecule (say N_2) an exchange of position of the atoms within the molecule is possible, whereas for an unsymmetrical molecule such as CO this is impossible. According to Ehrenfest and Trkal, the phase volumes, if calculated in the ordinary way, would come out to be too great by the factor 2 for diatomic molecules. They therefore subtract $\log 2$, since two exchanges are possible. For a molecule such as CH_4 , σ would be equal to 12.

Experiment so far is not sufficiently refined to enable a final judgment to be made as to whether the introduction of σ is correct or not.

The two gases CO and N_2 have almost exactly the same moment of inertia (and the same molecular weight), yet according to Eucken's† latest results, their chemical constants differ by much less than $\log 2$. Cox‡ endeavoured to calculate i for the halogens, but found that the available data were too inexact to enable him to arrive at any definite conclusion with regard to σ . For nitrogen, however, excellent agreement between the statistical and thermodynamical formulæ is obtained on taking $\sigma=2$. The agreement between i (dissociation) and i (vapour-pressure) for the same halogen is not very good, i (vapour-pressure) being about half as great as i (dissociation). In a recent note§ Cox recalculates i for chlorine, improving the agreement considerably.

The chief cause of error in work of this kind is the uncertainty in the values of λ_0 and λ_{∞} . For instance, there is a difference of some 30 per cent. in the figures for chlorine found by Henglein and by Trautz and Stäckel.

Again, lack of knowledge of possible allotropic changes is responsible for discrepancies of magnitude $q/4 \cdot 571T$, as Cox shows. q is the heat of transformation and T the temperature at which it occurs.

An account of some very detailed work on the constant i is contained in a recent paper by Eucken,|| where he discusses the gases $\text{H}_2, \text{N}_2, \text{O}_2, \text{Cl}_2, \text{I}_2, \text{NO}, \text{CO}, \text{HCl}, \text{HBr}, \text{HI}, \text{CO}_2, \text{H}_2\text{O}, \text{NH}_3$ and CH_4 . A new research into the molecular heats of several

* Zeit. für Electrochem., 25, p. 28 (1919).

† Zeit. für Phys., 29, p. 1 (1924).

‡ Proc. Camb. Phil. Soc., 21, p. 541 (1923).

§ Loc. cit., 22, p. 491 (1924).

|| Zeit. für Phys., 29, p. 1 (1924).

of these was published at the same time.* Direct data are thereby obtained for the calculation of the integral

$$\int_0^T \frac{dT}{T^2} \int_0^T C_v dT$$

Eucken uses the figures he obtains for i to deduce the moment of inertia J_i from formula (15), omitting σ , and compares this with the value $J_{opt.}$ obtained from the spectra. The differences are marked and show little regularity. Thus for O_2 , NO, HCl, HBr, HI, $J_i > J_{opt.}$, whereas for H_2 , N_2 , CO, CO_2 , H_2O , he finds the reverse. Up to the time of writing, no explanation of these irregularities has been suggested.

(3) GASEOUS DEGENERATION.

In the portion of this paper dealing with specific heats we have considered the falling-off, according to the quantum theory, of the rotational and vibrational molecular heats of diatomic gases with decreasing temperature. The experimental fact there mentioned was that in hydrogen (below 60° absolute) the molecular heat C_v resembled that of a monatomic gas in having the value $\frac{3}{2}R$, corresponding to translational energy alone. Tetrode† and others have attempted to apply the quantum theory to translations. At present the whole basis is very insecure. The method is to consider the thermal motions in a gas divided up into a spectrum of natural frequencies. The energy is then distributed among the natural frequencies according to the usual equation $\bar{U} = \frac{\varepsilon}{e^{K\varepsilon} - 1}$.

Planck‡ and Scherrer§ apply the quantum rules directly to the individual atoms, and show that their velocity and energy of translation can only acquire discrete values. Eucken|| has measured the molecular heats of hydrogen and helium at high pressures and at very low temperatures.

He finds that the molecular heat falls even below $\frac{3}{2}R$. Thus, for hydrogen

$T = 29.6^\circ$ abs.	$C_v = 3.20$
24.0°	3.02
21.2°	2.78
18.6°	2.70

The reading at 29.6° when recalculated by Berthelot's equation yields approximately $C_v = 2.98$, so that at lower temperatures C_v is even smaller than that of a perfect gas where the whole energy is translational.

Again, the greater the compression the lower the value of C_v for a given temperature.

The effect is sketched in a graph for two volumes, ($V_1 > V_2$).

* Zeit. für Phys. Chem., 112, p. 467 (1924).

† Phys. Zeit., 14, p. 212 (1913). Ann. der Phys., 38, p. 434 (1912).

‡ Berl. Ber., p. 653 (1916).

§ Göttingen Nachr., July 8, 1916.

|| Ber. Deut. Phys. Ges., 18, p. 4 (1916).

Nernst discusses this "degeneration" from the ideal gaseous state.

He postulates a special kind of rotation of the molecule not caused by collisions, but due to the transformation of the translational energy, presumably *per se*, into "rotational" energy. It is only necessary to remember that the frequency of the true molecular rotations existing at higher temperatures must be very much greater than that associated with this "degenerate rotation" to see how very speculative Nernst's ideas are.

If these "rotations" are to be quantized we must write for the energy in the degenerate state

$$U = \frac{3}{2} R \frac{\beta \nu}{e^{\beta/T} - 1},$$

so that C_v tends to zero for $T=0$. Support for some such conception is afforded by Eucken's observations, but it is difficult to follow Nernst in his view of degenerate rotation. It may be mentioned here that one of the chief points of the theory of

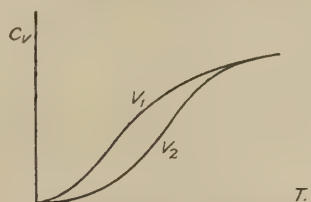


FIG. 4. THE "DEGENERATION" OF HYDROGEN (EUCKEN).

gaseous degeneracy lies in the possibility which springs from it of applying the Nernst Heat Theorem directly to gases.

Since the details of this are hardly germane to the purpose of the present essay, it will not be considered further.

Assuming, however, that such an application is justifiable, Nernst* deduces on a degeneracy basis a value for the chemical constant of monatomic gases. He finds

$$i = \log \frac{(4\pi m)^{3/2} h^{5/2}}{e h^3} \quad \dots \quad (16)$$

compared with Ehrenfest's and Trkal's

$$i = \log \frac{(2\pi m)^{3/2} h^{5/2}}{h^3}$$

The ratio

$$\frac{(4\pi)^{3/2}/e}{(2\pi)^{3/2}} = 1.015.$$

Experiment is hardly accurate enough yet to make a decision between the two.

For the sake of completeness, mention should be made of Lindemann's† adverse criticism of the whole theory of degeneracy in gases.

* Grundlagen des neuen Wärmesatzes (1918).

† Phil. Mag., 39, p. 21 (1920).

His argument is based almost entirely upon dimensional considerations. Rejecting degeneracy, he shows that if $C_p = \frac{5}{2}R$ down to the absolute zero, it might be possible to link up the chemical constant with radiation theory.

The most recent work on the subject is that of Bennewitz,* who sets out to find the general equation of state of an (ideal) degenerate gas, which shall not conflict with the Nernst degeneracy equation of energy

$$U = \frac{3}{2}RT \cdot \frac{1}{2}x \cdot \frac{e^x + 1}{e^x - 1} \quad \dots \dots \dots (17)$$

$$\left[x = \frac{\beta v}{T} = \frac{h^2 N^{\frac{1}{3}}}{4\pi m k} \cdot \frac{1}{TV^{2/3}}, V = \text{molar volume} \right]$$

and which satisfies

(a) The 1st and 2nd laws of Thermodynamics,

(b) The classical equation $pv = \frac{2}{3}U$ (for ideal gases),

(c) The Nernst Heat Theorem,

(d) The condition $\left(\psi + T \frac{d\psi}{dT} \right)_{T=0} = 0$ (ψ defined as below).

The equations found are

$$U = \frac{3}{2}RT\psi \quad \dots \dots \dots (18)$$

$$pv = RT\psi \quad \dots \dots \dots (19)$$

where ψ is a function of $\left(\frac{\text{constant}}{TV^{2/3}} \right) = f(x)$.

As a result, C_v is no longer equal to $\frac{3}{2}R$ for an ideal monatomic gas, but to

$$\frac{3}{2}R(1 - \alpha), \text{ where } \alpha = \frac{x}{\psi} \cdot \frac{d\psi}{dx}.$$

Similarly C_p becomes $\frac{5}{2}R \frac{1 - \alpha}{1 + \frac{2}{3}\alpha}$, so that the difference of the specific heats is no

longer independent of the temperature and equal to R as on the classical theory, but to $R \frac{(1 - \alpha)^2}{1 + \frac{2}{3}\alpha}$. Also the ratio $\gamma \left(= \frac{C_p}{C_v} \right)$ no longer has the value $\frac{5}{3}$, but

involves the degeneracy function ψ , and becomes equal to $\frac{5}{3} \frac{1}{1 + \frac{2}{3}\alpha}$. Bennewitz

discusses the limiting cases $T=0$ and $T=\infty$ in connexion with the problem of the existence of a zero-point energy.

* Zeit. für Phys. Chem., 110, p. 725 (1924).

The results may be tabulated for convenience :—

—	$T=0$	$T=0$	—	$T=\infty$	$T=\infty$
	Classical.	Deg.		Classical.	Deg.
C_v	$\frac{3}{2}R$	0	C_v	$\frac{3}{2}R$	$\frac{3}{2}R$
C_p	$\frac{5}{2}R$	0	C_p	$\frac{5}{2}R$	$\frac{5}{2}R$
$C_p/C_v=\gamma$	$\frac{5}{3}$	1	$C_p/C_v=\gamma$	$\frac{5}{3}$	$\frac{5}{3}$
C_p-C_v	R	0	C_p-C_v	R	R

Thus the degenerate values pass over into the classical values at high temperatures. In this connexion the author discusses a kind of Correspondence Principle analogous to that of Böhr in the quantum theory, in which "degenerate" thermodynamics can be considered to become classical for large values of T .

According to Bennewitz, the equation for the chemical constant is

$$i = \log R\psi(0) - \frac{3}{2} \log C - \frac{5}{2} + \frac{1}{R\psi(0)} \int_0^0 \log x \frac{dC_v}{dx} dx \quad . \quad . \quad . \quad (20)$$

It is interesting to verify that this reduces to Nernst's expression (17) for ordinary (high) temperatures.

For T large $\psi(0)=1$

$$C = \frac{h^2 N^{2/3}}{4\pi m k}$$

$$\int_0^0 \log x \frac{dC_v}{dx} dx = \frac{3}{2} R [\log x]_0^0 + \frac{3}{2} R \left[\frac{x e^x}{e^x - 1} \right] - \frac{3}{2} R [\log e^x - 1]_0^0 = \frac{3}{2} R$$

$$\text{Thus } i = \log Nk - \frac{3}{2} \log (h^2 N^{2/3} / 4\pi m k) - \frac{5}{2} + \frac{3}{2} = \log \frac{(4\pi m)^{3/2} h^{5/2}}{e h^3}$$

as already given (equation (16)).

There remains a recent Paper of Eucken's* to be considered. He establishes the thermodynamical relations for chemical equilibrium in twenty-one typical homogeneous and heterogeneous reactions, and obtains the constant i_K corresponding to i in the vapour-pressure equation.

The results are not consistent, but the point of interest here is that the equation $i_K = \Sigma i$, as demanded by Nernst's Theorem, is not satisfied.

DISCUSSION.

Capt. A. C. G. EGERTON : Mr. Rawlins has given a very interesting résumé of the position of theory in respect of the specific heat of the solid and gaseous states. He mentions that in my Paper to the Physical Society last year I omitted to mention the work of Ladenburg and Minkowski on the vapour pressure of sodium and potassium, and the irregular values of the chemical constants of those metals. The measurements on which they base those values are, however, not direct vapour-pressure measurements. We have made a series of measurements on the vapour pressures of sodium and potassium, and although the work is not quite completed, the evidence so far is that there is nothing irregular in the value of the constants for these two metals.

* Zeit. für Phys., 29, p. 36 (1924).

Another point of interest, I think, in connection perhaps with difficulties respecting theories of specific heat of gases is the existence of absorption bands due to the temporary formation of diatomic molecules in vapours where, from ratio of specific heat measurements and also vapour-pressure measurements, there is no evidence of any but monatomic molecules. Franck and others have investigated this matter in the case of mercury.

Dr. D. OWEN said he thought it a very good thing that the Society should have Papers of the present kind from time to time, in spite of the great difficulty of the subject matter, which is somewhat strange to the majority of experimental physicists. Great Britain has of late tended to lag behind continental countries in mathematical physics, and therefore the school with which Capt. Egerton is associated at Oxford, and that which the author is forming at Cambridge, are of great importance, and deserve the best wishes of British physicists. Dr. Owen added that the conception of the chemical constant i merely as a constant of integration is a little unsatisfying. Is it possible to form a more concrete conception of it?

AUTHOR'S reply: I am grateful to Captain Egerton for his remarks. It is satisfactory to learn that recent work tends to show that the behaviour of Na and K is normal with respect to the constant i_0 . This naturally is to be welcomed as rendering it needless to make somewhat arbitrary assumptions as to the relative quantum weights of solid and vapour.

In reply to Dr. Owen: While sympathizing with his wish for a more physical picture of i , may I venture to suggest that this quantity suffers from the same inherent kind of "aloofness" as entropy; which latter only received a satisfactory physical basis at the hands of Carathéodory (Math. Ann. 61, 355, 1909)? The views of Prof. Lindemann (referred to in my Paper) are very suggestive.

Dr. ALLAN FERGUSON (communicated): I should like to express my thanks to Mr. Rawlins for his very clear summarising of this new knowledge. Very many of us have felt that the light cast upon physico-chemical problems by the chemical constant has been rather less than that of a farthing candle. Mr. Rawlins' efforts have considerably increased the intensity of that illumination.

My own interest in the chemical constant is indirect. As Mr. Rawlins has pointed out, the value of Q_0 is subject to considerable error. Van't Hoff's reaction isochore

$$\frac{d(\log K)}{dT} = \frac{Q}{RT^2}$$

cannot be integrated until we know Q as a function of T . Van't Hoff's equation has a rational basis, but no such basis has been suggested for the *velocity* constants k_1 and k_2 for, say, a bimolecular reaction. Arrhenius has put forward an empirical relation

$$\frac{d(\log k)}{dT} = \frac{a}{RT^2}$$

where a is constant. This leads to

$$\log k = A - \frac{B}{T},$$

but a plot of $1/T$ against $\log k$ shows in general distinct curvature. I am at present investigating other relations between $\log k$ and T , some of which seem promising. These relations, together with the known relation between K , k_1 and k_2 , suffice to give Q as a function of T having at least a semi-rational basis. These relations may serve to test the usual "Planckian" equation for Q ,

$$Q = Q_0 + \frac{h\nu_0}{k} R \frac{e^{\frac{h\nu_0}{kT}}}{1 - e^{\frac{h\nu_0}{kT}}} - 3T,$$

at ordinary temperatures, and possibly to form a basis for reliable values of Q_0 , although extrapolations are always doubtful.

XXII.—ON THE "HYPERBOLA" METHOD FOR THE MEASUREMENT OF SURFACE TENSIONS.

By A. FERGUSON, M.A., D.Sc., and I. VOGEL, B.Sc.

ABSTRACT.

When a liquid lies between two plates inclined to one another at a small angle its surface has a hyperbolic section, from measurement of which the surface tension can be calculated. The method has long been known, but has recently been improved by Grünmach. Errors arise, however, from the difficulty of determining the horizontal and vertical axes of co-ordinates, and according to the present Paper this difficulty is met by plotting two linearly related functions of the observations, the surface tension being deduced from the co-ordinates of the resulting mean straight line and the angle between the plates. The latter may be measured either directly or by calibration with a liquid of known surface tension.

THE surface tension of a liquid may be deduced from measurements made on the curve assumed by a liquid after rising between two vertical plates inclined to each other at a small angle. The values so obtained are not usually very exact, and the method, for a good many years past, has been relegated to the comparative obscurity of a laboratory illustration of the principles of surface tension.

In a series of Papers,* of which the principal one is entitled "*Über ein neuen Plattenapparat zur Bestimmung von Kapillaritätskonstanten nach der Steighöhenmethode*," Grünmach has introduced into the method certain modifications which are intended to simplify its technique and increase its accuracy. The word "new" in the title just given may presumably be used in virtue of these modifications, but the method itself is of very respectable antiquity. It was described, and the hyperbolic nature of the curve was recognised, by Brook Taylor† and by Hauksbee‡ in 1712-13. The apparatus and the curve are admirably figured in s' Gravesande's§ "*Mathematical Elements of Natural Philosophy*," and the proof given by Muschenbroek|| may be quoted even now as one of the most compact proofs of the nature of the capillary curve.

Apart from any small corrections concerning the nature of the capillary surface, the manner in which the hyperbolic nature of the surface-curve depends on the smallness of the angle between the plates is easily investigated. Thus, assuming a

* Grünmach, *Physik. Zeitschr.*, 11, 980 (1910). Grünmach, *Zeitschr. Instrumentenk.*, 30, 366 (1910). Grünmach and Bein, *Zeitschr. Instrumentenk.*, 39, 195 (1919).

† *Phil. Trans.*, 27, 538 (1712).

‡ *Phil. Trans.*, 28, 151 and 153 (1713).

§ English translation by Desaguliers, 4th edition (1731).

|| *Introductio ad Philosophiam Naturalem*, Tom. 1, p. 376 (1762). "*Si ambo specula plana, ad solum perpendicularia, uno latere jungantur, ut se contingant: opposito latere distiterint, angulumque forment, haec imposita Aquae, eam altius attollent, in locis, quibus specula sint propria; minus ubi specula plus distant; elevatae aquae inter specula superficies formabit curvam, Hyperbolam, cujus Asymptotae erint speculi latera CD, DE; est enim Da ad Db ut distantia speculorum aa' ad bb': sed est altitudo Bb ad Aa in ratione inversa distantiorum in his locis; sive est uti Da ad Db: adeoque erit Da x Aa = Db x Bb. Quae est proprietas Hyperbolae.*" (See Fig. 1).

zero-contact angle with glass (γ being the surface tension of the liquid, and φ the angle between the plates), we have for the vertical component of the tensions along AB and $A'B'$ the value $2\gamma ds \cos \theta$ or $2\gamma dx$. The difference of the vertical components on AA' and BB' is

$$\gamma \varphi dx \cdot \frac{d}{dx}(x \sin \theta).$$

Hence, if the area of the base is δA , we have

$$2\gamma \delta x = g \rho y \delta A + \gamma \varphi \frac{d}{dx}(x \sin \theta) \delta x \quad \dots \dots \dots (1)$$

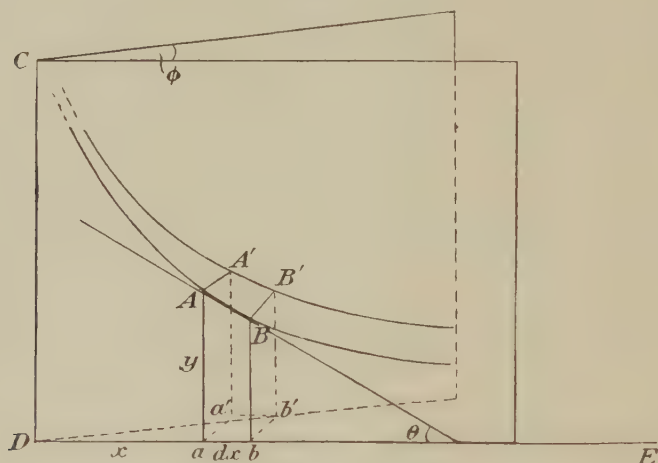


FIG. 1.

Including terms of the order φ^2 , we have for δA

$$\delta A = \varphi x \delta x,$$

and (1) then becomes

$$2\gamma = g \rho \varphi xy + \gamma \varphi \frac{d}{dx}(x \sin \theta) \quad \dots \dots \dots (2)$$

Approximately

$$xy = \frac{2\gamma}{g \rho \varphi} = K \text{ (say) ;}$$

and hence

$$\tan \theta = -\frac{dy}{dx} = \frac{K}{x^2};$$

or, taking the positive sign for $\sin \theta$,

$$\sin \theta = \frac{K}{\sqrt{K^2 + x^4}}$$

This gives

$$\frac{d}{dx}(x \sin \theta) = y \cdot \frac{y^2 - x^2}{(y^2 + x^2)^{3/2}}$$

which value, substituted in (2), together with the approximate value

$$\gamma = \frac{g \rho \phi xy}{2}$$

leads immediately to the equation

$$2a^2 \equiv \frac{2\gamma}{g \rho} = \phi xy \left\{ 1 + \frac{\phi}{2} \cdot y \cdot \frac{y^2 - x^2}{(y^2 + x^2)^{3/2}} \right\} \quad \dots \dots \dots (3)$$

Equation (3) shows clearly the conditions under which the hyperbolic formula is valid. If ϕ be sufficiently small, we have

$$xy = \frac{2a^2}{\phi} = K \quad \dots \dots \dots (4)$$

which is the relation usually employed. If, however, we find a systematic variation in K , a plot of two new variables (X , Y), given by

$$xy = Y \text{ and } xy^2 \cdot \frac{y^2 - x^2}{(y^2 + x^2)^{3/2}} = X,$$

should yield a straight line

$$Y + \frac{\phi}{2} X = \frac{2a^2}{\phi} \quad \dots \dots \dots (5)$$

whose slope and intercept determine a^2 and ϕ . In all ordinary instances equation (4) is sufficiently exact.

In Grünmach's earlier apparatus, the values of x and y are determined, by means of a kathetometer, relative to the axes DE and DC of Fig. 1. The "constant" xy is not at all constant, but in certain instances shows indications of the systematic variation just mentioned. Table I below, which is taken from Grünmach's Paper sufficiently illustrates this point.

TABLE I.

Pure oleic acid. Curve 1.			Temp. 20°C. Curve 4.		
x	y	xy	x	y	xy
25	11.6	290	35	19.5	684.3
30	9.7	291	40	17.1	684
35	8.5	297.5	45	15.1	679.5
			50	13.7	685
			55	12.4	682
			60	11.6	696
			65	10.7	695.5
			70	10.0	700
	Mean ...	293		Mean ...	688.3

so that a plot of xy as Y against x yields a straight line whose intercepts give the desired constant K . But it is not necessary to know the position of either x or y .

Table II below shows in detail the result of an experiment made on distilled water :—

TABLE II.—*Water—Experiment 1.*

x cms.	y cms.	X	Y	Y/X	$(x+h)$	$(y+k)$	$(x+h) (y+k)$
14.533	14.744	4.533	9.271	2.045	—1.306	11.941	15.59
14.000	11.257	4.000	5.784	1.446	—1.839	8.454	15.55
13.500	9.404	3.500	3.931	1.123	—2.339	6.601	15.44
13.000	8.269	3.000	2.796	0.932	—2.839	5.466	15.52
12.500	7.419	2.500	1.946	0.778	—3.339	4.616	15.41
12.000	6.873	2.000	1.400	0.700	—3.839	4.070	15.62
11.500	6.389	1.500	0.916	0.611	—4.339	3.586	15.56
11.000	6.029	1.000	0.536	0.536	—4.839	3.226	15.61
10.500	5.716	0.500	0.243	0.486	—5.339	2.913	15.55
10.000	5.473	0.000	0.000	0.000	—5.839	2.670	15.59
9.500	5.256	—0.500	—0.217	0.434	—6.339	2.453	15.55
9.000	5.068	—1.000	—0.405	0.405	—6.839	2.265	15.49
8.500	4.921	—1.500	—0.552	0.368	—7.339	2.118	15.54
8.000	4.779	—2.000	—0.694	0.347	—7.839	1.976	15.49
7.500	4.675	—2.500	—0.798	0.319	—8.339	1.872	15.61
7.000	4.561	—3.000	—0.912	0.304	—8.839	1.758	15.54
6.500	4.451	—3.500	—1.022	0.292	—9.339	1.648	15.39
6.000	4.377	—4.000	—1.096	0.274	—9.839	1.574	15.49
5.500	4.310	—4.500	—1.163	0.258	—10.339	1.507	15.58
5.000	4.248	—5.000	—1.225	0.245	—10.839	1.445	15.63
						Mean ...	15.54

The graph of Y/X against X gives the curve of Fig. 2.

The constants of this line are

$$m=5.839, c=2.670;$$

whence

$$h=-15.84, k=-2.803.$$

The mean value of K is 15.54, and by measurement with the microscope

$$\phi=0.1190 \div 12.40.$$

Hence, substituting in (4), we have at a temperature of 14.1 C.

$$\gamma=73.15 \text{ dyne cm.}^{-1}.$$

[In succeeding records we restrict ourselves to giving the separate values of the constant only; it is the magnitude of the variation of this quantity which serves initially as a criterion of the trustworthiness of the method.]

Water—Experiment 2.

Values of K —

19.03, 19.14, 19.04, 18.95, 19.12, 19.03, 19.08, 19.02, 19.07, 19.03, 19.05.

Mean 19.05.

$$\phi=0.09750 \div 12.62.$$

Temp. 23.9°C.

$$\gamma=72.19 \text{ dyne cm.}^{-1}.$$

Water—Experiment 3.

Values of K —

20.31, 20.56, 20.10, 20.60, 20.06, 20.34, 19.81, 20.25, 19.88, 20.05, 19.83, 20.06,
19.65, 19.83, 19.64, 19.87.

Mean 20.05.

$$\varphi = 0.09425 \div 12.62.$$

Temp. 14.9°C.

$$\gamma = 73.45 \text{ dyne cm.}^{-1}.$$

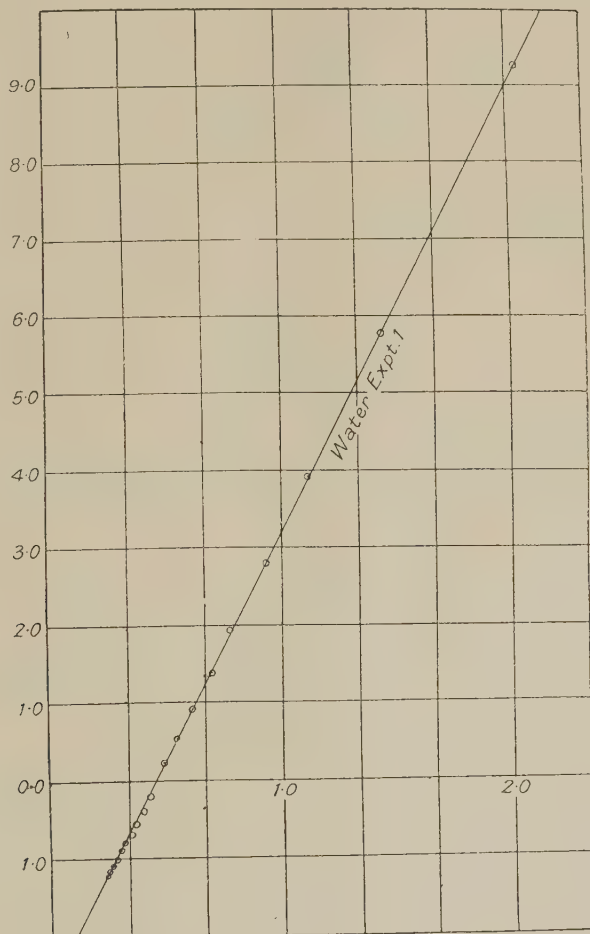


FIG. 2.

*Benzene—Experiment 1.*Values of K —

8.965, 8.965, 9.062, 9.052, 9.063, 9.019, 8.965, 9.033, 9.022, 9.108, 9.122, 9.152, 9.107, 9.062, 9.170, 9.080.

Mean 9.059.

$$\varphi = 0.09500 \div 12.62.$$

Temp. 16.3°C.

$$\gamma = 29.34 \text{ dyne cm.}^{-1}.$$

*Benzene—Experiment 2.*Values of K —

8.003, 8.219, 8.263, 8.241, 8.212, 8.296, 8.168, 8.274, 8.248, 8.238, 8.287, 8.249, 8.177, 8.211, 8.266.

Mean 8.225.

$$\varphi = 0.1030 \div 12.40.$$

Temp. 16.0°C.

$$\gamma = 29.39 \text{ dyne cm.}^{-1}.$$

*Benzene—Experiment 3.*Values of K —

8.381, 8.297, 8.339, 8.337, 8.372, 8.371, 8.299, 8.361, 8.339, 8.396, 8.327, 8.375.

Mean 8.348.

$$\varphi = 0.1010 \div 12.40.$$

Temp. 15.4°C.

$$\gamma = 29.26 \text{ dyne cm.}^{-1}.$$

Collecting these results and assuming a temperature coefficient of 0.15 dyne cm.⁻¹ (degree Cent.)⁻¹ for water, and 0.13 dyne cm.⁻¹ (degree Cent.)⁻¹ for benzene, we find values for γ in fair agreement with those found by other methods.

TABLE III.

Water.			Benzene.		
Temp. θ	γ_{θ}	$\gamma_{15^{\circ}}$	Temp.	γ_{θ}	$\gamma_{20^{\circ}}$
14.1	73.15	73.01	16.3	29.34	28.85
23.9	72.19	73.53	16.0	29.39	28.87
14.9	73.45	73.43	15.4	29.26	28.66
Mean	...	$\gamma_{15^{\circ}}=73.32$		Mean	... $\gamma_{20^{\circ}}=28.74$

We now turn to the results obtained by the comparative method. Benzene was used as the standard liquid, the surface tension of benzene being taken as 28.88 dyne cm.⁻¹ at 20.0°C.* The values of h and k being determined as described we find the values given below for the constant K .

* Richards and Carver, J. Amer. Chem. Soc., 43, 827 (1921).

Benzene—Experiment 4.

Values of K —

10.28, 10.15, 10.19, 10.15, 10.18, 10.16, 10.12, 10.15, 10.19, 10.02, 10.13, 10.00, 10.17, 10.17, 10.21.

Mean 10.15.

This leads at once from equation (4) to the value

$$\phi = 6.612 \times 10^{-3}.$$

The results for three experiments with toluene are given below. The plates were taken down, cleaned, dried and reassembled between each experiment.

Experiment 1.

Values of K —

10.09, 10.05, 10.04, 10.06, 10.06, 10.05, 10.08, 10.10, 10.04, 10.12, 10.17, 9.98, 10.05, 10.14, 10.06, 10.00.

Mean 10.07.

$$\phi = 6.612 \times 10^{-3}.$$

Temp. 21.8°C.

$$\gamma = 28.23 \text{ dyne cm.}^{-1}.$$

Experiment 2.

Values of K —

10.02, 9.845, 9.982, 9.975, 9.974, 9.941, 9.977, 10.02, 9.885, 9.763, 9.916, 9.898, 9.930, 9.945, 9.970, 9.868, 9.981.

Mean 9.935.

$$\phi = 6.612 \times 10^{-3}.$$

Temp. 23.8°C.

$$\gamma = 27.85 \text{ dyne cm.}^{-1}.$$

Experiment 3.

Values of K —

10.02, 9.936, 9.946, 9.939, 9.980, 9.983, 9.987, 9.932, 9.894, 9.987, 9.926, 10.10, 10.15, 9.979, 10.18.

Mean 9.996.

$$\phi = 6.612 \times 10^{-3}.$$

Temp. 20.2°C.

$$\gamma = 28.02 \text{ dyne cm.}^{-1}.$$

The results for toluene and their reduction to γ_{20° by means of a known temperature coefficient are exhibited in Table IV.

TABLE IV.

Temperature coefficient assumed = 0.15 dyne cm.⁻¹ (degree Cent.)⁻¹.

Temp. θ	γ_θ	γ_{20°
21.8	28.23	28.50
23.8	27.85	28.42
20.2	28.02	27.99
	Mean	$\gamma_{20^\circ} = 28.30$

The mean value given above is in fair agreement with the value 28.43 dyne cm. obtained by Richards and Carver. A number of the straight lines from which the values of h and k are determined are shown in Fig. 3, and it will be seen that they are very accurately rectilinear, the coefficient being determined without any trace of ambiguity.

It is no easy matter to obtain consistent surface tension measurements in a

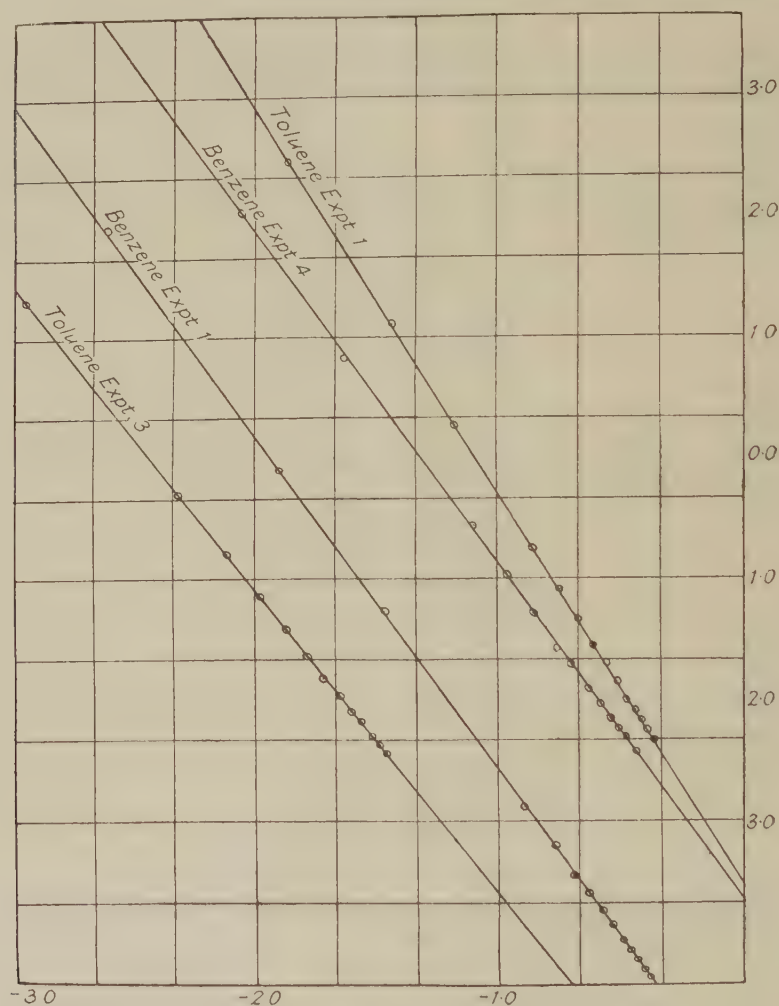


FIG. 3.

London atmosphere, especially when the method employed involves the handling and exposure of large quantities of liquid. Some of our experiments, notably those with water, gave values of K which in any one experiment were perfectly self-consistent, but which gave low and irregular values for the surface tension. These irregularities are to be attributed to atmospheric impurities, for it is the experience

of one of us that the method, given in its primitive form as a laboratory experiment, can be depended to give values correct to about 1 per cent. in a pure atmosphere.

When the observations are reduced in this manner, we feel that the technique of the method is considerably more accurate than the technique employed by Grünmach. It has one of the limitations of the capillary rise method, in that it assumes that the liquids under experiment have a zero contact angle. Moreover, the gain of precision which this method of reduction entails is accompanied by a corresponding increase in the time spent. A good deal of this time and labour might be saved if the front plate be ruled with one horizontal and a series of vertical lines exactly 1 cm. apart, the vertical lines being marked off in millimetres. The instrument then becomes one which makes very little demand on the resources of a technical laboratory—a point of some importance in technological practice—the only accessories needed being a hand lens for reading off the y -co-ordinates to the nearest tenth of a millimetre, and a sample of some liquid of known surface tension for standardisation.

DISCUSSION.

Dr. J. H. VINCENT suggested that in addition to avoiding errors of displacement in the co-ordinate axes, the method might yield a correction for errors in the verticality of the line of intersection of the plates.

Mr. T. SMITH said that in introducing his Paper the author had referred to lens-system formulæ which could be transformed so as to yield linear graphs, and had suggested that the co-ordinates of the resulting mean straight lines would give average results for the observations in which they were based. It must be remembered, however, that geometrical optics represents only an approximation to the physical facts, and that the values obtained in different regions of a range of observations have very different probabilities of error. In practice the mean adopted must be a weighted mean, which is not provided by the linear-graph method.

XXIII.—THE APPLICATION OF RADIOGRAPHY TO THE STUDY OF CAPILLARITY.

By E. A. OWEN, *M.A., D.Sc.*, and A. F. DUFTON, *M.A., D.I.C.*, Physics Department,
National Physical Laboratory.

ABSTRACT.

The X-ray shadow of a tube has previously been used for determining the diameter of the bore. The present investigation was designed to test the suitability of a similar method for capillarity measurements, and observations were made of the rise of mercury in copper and steel tubes and between vertical copper plates. The results were satisfactory.

THE radiographic method has been successfully employed for the measurement of the internal diameters of tubes.* It occurred to the authors that the method might prove useful for the study of problems in capillarity and a few experiments, a brief account of which is given in this Paper, were carried out to investigate it from this point of view.

Avogadro† determined the capillary constant for mercury by measuring the rise in a copper tube 2.80 mm. in diameter, well amalgamated in the interior, and found it to be 5.56 sq. millimetres. This value is lower than those determined subsequently by other methods.

In repeating this experiment, two tubes having internal diameters of 1.62 mm. and 2.09 mm. respectively were employed. The tubes were well amalgamated and thoroughly cleaned before being introduced into a trough of distilled mercury, in which they were held when the radiograph shown in Fig. 1 was taken. The X-ray bulb used for the work had a tungsten anticathode and was operated at 2 milliamperes and 120 kilovolts. The tubes were situated a metre away from the X-ray bulb with the photographic plate or film fixed close behind them. The exposure under these conditions was about three minutes.

The values of the surface tension of mercury at 17°C. (room temperature) deduced from the measurement of the radiograph are included in Table I. The two tubes gave quite consistent results.

TABLE I.

Diameter of tube (<i>d</i>).	Capillary rise (<i>h</i>).	$a^2 = \frac{d}{2} \left(h + \frac{d}{6} \right)$	<i>t</i> 17°C.
1.62 mm.	8.69 mm.	7.27 sq. mm.	484 dynes/cm.
2.09	6.65	7.31	486
Mean value			485 dynes/cm.

A further determination of the surface tension of mercury was made by radiographing the rise of mercury between two flat vertical copper plates inclined at

* See Anderson and Barr, *Journ. Scient. Instr.*, I, 1, p. 9, October (1923).

† Cf. Bashforth and Adams, *Capillary Action*, p. 8.

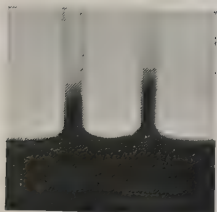


FIG. 1.



FIG. 2.

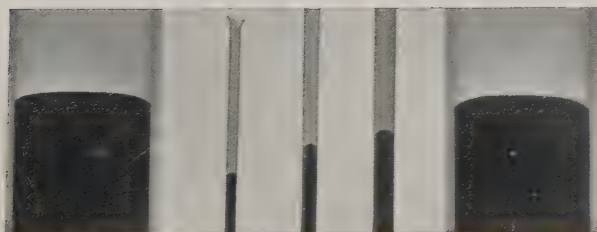


FIG. 3.

small angle to one another. The radiograph shown in Fig. 2 was obtained with plates inclined at an angle of 0.0284 radian. The mercury surface appears as a rectangular hyperbola whose equation is $xy=251$ sq. mm. This gives the value

$$a^2 \equiv \frac{2T}{\rho g} = 0.0284 \times 251 = 7.13 \text{ sq. mm.}$$

and

$$T_{17^\circ\text{C.}} = 474 \text{ dynes per cm.}$$

The mean value of the surface tension of mercury at 17°C. given by these methods is 480 dynes per cm. It is in tolerable agreement with the value of 465 dynes per cm. at 20°C. obtained by Harkins and Grafton* but is considerably lower than the value of 547 dynes per cm. at 17.5°C. given by Quincke.†

Fig. 3 shows a radiograph of the depression of mercury in three steel tubes. The tubes were fixed in a horizontal tube connecting two glass reservoirs of diameter 18 mm. The level of the mercury in the reservoirs served as a surface of reference. The results of the measurement of the radiograph are given in Table II, a correction of 0.06 mm. having been made for the capillary depression in the reservoirs.

TABLE II.

Diameter of tube (d).	Capillary depression (h).	$a^2b = \frac{d}{2} \left(h + \frac{d}{6} \right)$
1.21 mm.	10.56 mm.	6.51 sq. mm.
1.83	6.63	6.34
2.52	4.80	6.58
Mean value		6.48 sq. mm.

From the mean value of a^2b ($=6.48$ sq. mm.) and the value of a^2 ($=7.21$ sq. mm.) obtained in the first two experiments, the value of b , that is $\cos(\pi - \omega)$, where ω is the angle of contact, works out to be 0.899, so that the angle of contact between mercury and steel is 154° approximately.

The above examples serve to indicate the possibilities of the method. It can be employed for the solution of problems to which the usual methods of measuring surface tension are inapplicable and it has an advantage over these methods in that a permanent record is obtained which can be examined at leisure.

The authors do not intend to pursue the subject further. They have directed attention to the method in the hope that it will be of interest to those engaged in the study of capillarity.

In conclusion, they wish to take this opportunity of thanking Mr. T. A. Chalmers for his help in taking the radiographs.

DISCUSSION.

Dr. D. OWEN asked if the authors had tried radium as a substitute for X-rays, and if so with what results. In regard to the determination of the surface tension of mercury by ascent of a copper tube, it appeared that the results by this method agree with those obtained by more usual methods; so that the degree of contamination of the mercury by copper did not appear to affect the value appreciably. The value of the angle of contact using a steel tube

* Journ. Amer. Chem. Soc., 42, 2534 (1920).

† Pogg. Ann., 105, 35 (1858).

comes out rather large: it would be of interest to have particulars of the method of cleansing the tube.

Mr. J. E. CALTHROP: I should like to ask Dr. Owen if the value of h for a tube showing capillary rise was measured from the "bottom" of the meniscus, because it is not evident from the photograph that such a measurement is possible. Also, in calculating the capillary rise or fall was any allowance made for the fact that the photographic plate was further from the X-ray source than the column casting the shadow? What was the approximate distance of the plate from the centre of a capillary tube?

Dr. V. E. PULLIN (communicated): The following application of radiography, somewhat similar to the work described by Dr. Owen and Mr. Dufton, was recently investigated in my laboratory, and will probably be of interest to the Society.

A manufacturing firm applied for information as to the possibility of reading the height of a mercury column in a steel tube used as a piezometer, the walls of the tube being 4 mm. thick and the bore 8 mm., and the tube was contained in a water-jacket.

It was found possible to obtain a sharp outline of the mercury surface in such a tube distant 45 inches from the focus of the X-ray tube, with an exposure of 10 seconds, using 5 milliamperes at 150 kilovolts.

By attaching to the steel tube, in the plane containing the axis of the tube, a lead screen having fine holes drilled through it at intervals of 1 mm., it was possible to obtain in a radiograph a record of the mercury level and a scale for reading its height.

Dr. OWEN said that the rays from radium had not been tried. He was of opinion that with such penetrating radiation the definition of the shadow would not be satisfactory for the purpose of measurement. As to the method of cleaning the steel tube, the inner surface was first polished by passing string covered with fine emery powder to and fro through the tube. The emery was removed by passing another length of string steeped in distilled water through the tube. Distilled water was afterwards passed through the tube, which was finally washed and dried with alcohol solution.

In reply to Mr. Calthrop, the value of " h " was obtained from the curved surface of the meniscus—the "bottom" of the meniscus in the tubes showing capillary rise, and the "top" of the meniscus in the tubes showing capillary depression. The definition of the meniscus in Fig. 1. had suffered in the reproduction, but the original could be measured to the required degree of accuracy. In calculating the values of surface tension allowance had in each case been made for magnification. This was determined either from the external dimensions of the tube and its shadow, or from the distances of the photographic plate from the object and the source. The distance between the plate and the centre of the capillary tube varied in the different experiments. In the experiment shown in Fig. 1 it was 10 mm. approximately.

XXIV.—THE EFFECTS OF TORSION UPON THE THERMAL AND ELECTRICAL CONDUCTIVITIES OF ALUMINIUM, WITH SPECIAL REFERENCE TO SINGLE CRYSTALS.

By J. E. CALTHROP, *M.A., M.Sc.*, East London College.

ABSTRACT.

An attempt has been made to find the changes produced by torsion in the conductivities of single aluminium crystals, and of the annealed and hard aluminium wires from which the crystals are prepared. The hard wire gave a decrease of a few parts in a thousand in the thermal conductivity, but no change greater than one part in 1,000 has been found in crystal wires. The decreases in the electrical conductivities, of the order of a few parts in 10,000, appear to be almost the same for all specimens.

I. INTRODUCTION.

THE effects of strain upon the conductivities of metals are interesting from the point of view of the Wiedemann-Franz law, by which the ratio of the conductivities should remain constant at constant temperature. Bridgman* has investigated very thoroughly the effects of pressure and tension upon a large number of metals, and has found that the above law is not obeyed. For example, for tension upon aluminium, the metal in which we are at present interested, the changes in the specific conductivities, taken as unity, are :—

Thermal conductivity, -3.8×10^{-6} per kg./cm.²,

Electrical conductivity, -1.3×10^{-6} per kg./cm.²,

which values are corrected for changes in dimensions. The changes due to hydrostatic pressure are about five times greater than these.

The changes produced by torsion have been investigated by Smith,† and by Prof. Lees and the present author,‡ who agree in finding small decreases in both conductivities, the thermal changes being greater than the electrical. Smith took the changes to be proportional to the twist, and Calthrop as proportional to the square of the twist.

In the present Paper are described the results of tests, which have been made upon a hard wire, an annealed wire, and upon single crystals, prepared from similar hard wires. For the preparation of the crystals I am very much indebted to the kindness of Prof. H. C. H. Carpenter and Miss C. F. Elam, of the Royal School of Mines.

II. PREPARATION OF THE SPECIMENS.

The composition of the aluminium used was : Al, 99.6 per cent. ; Fe, 0.2 per cent. ; Si, 0.2 per cent. Other impurities were negligible.

The annealed wire was prepared by being kept for three minutes at 400°C., and then being allowed to cool gradually during five hours, according to instructions to be found in a book, "Aluminium and its Alloys," by C. Grard.

* P. W. Bridgman, *Proc. N.A.S.*, Vol. 59, No. 6 (1923).

† Smith, *Phys. Rev.*, 28, pp. 107-121 (1909).

‡ C. H. Lees and J. E. Calthrop, *Proc. Phys. Soc.*, Vol. 35, p. 225 (1923) ; Vol. 36, p. 168 (1924).

Miss Elam has personally prepared the single crystals by methods which have been fully described.*

After a preliminary heat treatment to remove hardness and to render the crystals equi-axed, a metal wire about 12 in. long is strained by tension to produce a 2 per cent. extension on a length of 3 in. The wire is then kept at a temperature of 550°C. for six hours, and the crystals finally etched with a 10 per cent. solution of caustic soda. They are so soft that great care is required to prevent strain, especially in the process of winding on the platinum coils used in the thermal measurements.

III. METHOD FOR THERMAL CONDUCTIVITY.

It is not proposed to describe the method in detail, as this has been done in the earlier Papers. The essence of the method is as follows:—

The wire to be tested is held in water-cooled clamps, which form the ends of a water-cooled, cylindrical chamber. Heat is supplied to the centre of the wire by means of a current in a manganin coil, and the temperatures at two points on one side of the heater are measured by two insulated platinum thermometers, wound round the test wire. A Callendar-Griffiths Bridge is used for measuring each resistance separately, the difference in the resistances, or the resistance of a coil which gives the variation of the temperature of the case.

The accuracy usually attained is that of one part in 1,000, but as the maximum length of the single crystals is only about 10 cms., it was thought well to reduce the lengths of the platinum thermometers, so that the accuracy for the single crystals is 0.15 per cent.

IV. THEORY OF THE METHOD.

It has been shown that:—

$$H = (qK \cdot \cosh ax_0 + hs \cdot \sinh ax_D) \frac{v_B - v_A}{\sinh ax_B - \sinh ax_A} \cdot \frac{ab}{\sinh ab}$$

where

H = Total supply of heat to half the wire.

q = Area of section of the wire.

K = Thermal conductivity.

h = Emissivity of the wire.

$a^2 = \frac{ph}{qK}$, where p is the perimeter of the wire.

x_0 = The distance of the near end of the heating coil from the clamp.

$x_D = x_0 + \frac{1}{3}(x_C - x_0)$, where x_C = distance of the centre of heating coil from clamp.

v_B, v_A = Temperature excesses at distances x_B and x_A from the clamp.

s = Half the area of the wire covered by the heating coil.

$2b$ = Length of wire covered by each of the platinum thermometers.

If S is the resistance of half the heating wire and the current is A amperes,

$$H = \frac{SA^2}{4.18} \dots \dots \dots (2)$$

* Carpenter and Elam, Proc. Roy. Soc., A., pp. 329-353 (1921); J. of Iron and Steel Inst., No. 1, 107, p. 175 (1923).

also v_B and v_A may be expressed in terms of the platinum resistances at the temperature of the case, R_0, r_0 , and those during heating, R_1, r_1 . Thus :—

$$v_B - v_A = \frac{35}{34} \cdot \frac{1}{\gamma} \left(\frac{R_1}{R_0} - \frac{r_1}{r_0} \right) \dots \dots \dots (3)$$

γ is the temperature coefficient of resistance for platinum, calculated from the resistance at the mean case temperature 15°C ., and a reduction of 1 cm. from the 35 cms., the usual length of the platinum thermometer, is made for the portion soldered to the copper leads.

Finally, from (1), (2) and (3)—

$$\left(qK + h s x_D \frac{\sinh ax_D}{ax_D} \cdot \frac{1}{\cosh ax_0} \right) \frac{a \cosh ax_0}{\sinh ax_B - \sinh ax_A} \cdot \frac{ab}{\sinh ab} = \frac{\gamma S A^2}{4 \cdot 34 \left(\frac{R_1}{R_0} - \frac{r_1}{r_0} \right)} \quad (4)$$

h has been taken as $0 \cdot 0003 \cdot \frac{ab}{\sinh ab}$ may be taken as unity. The constant $4 \cdot 34$ becomes slightly greater for a coil smaller than 35 cms. K may easily be calculated from (4).

V. METHOD OF OBSERVATION.

In measuring the thermal conductivity, time was given for the heating current to become steady, when the resistance of the case-coil, the resistance of the hot thermometer, and the difference in the resistances of the hot and cold thermometers were read in this order. The heating current was then measured to one part in 10,000, by comparing the fall of potential it produced in a fixed length of manganin wire with that of a standard cell, and then it was switched off. After about ten minutes, the resistances were read in the reverse order.

Readings for no twist and for two twists were usually taken one day, and again for no twist after the wire had been left untwisted all night.

VI. METHOD FOR ELECTRICAL CONDUCTIVITY.

In order to avoid any possible differences in temperature coefficients, the resistances of two wires of the same kind were compared by the ordinary potentiometer method. The fall of potential down the wire to be twisted was balanced

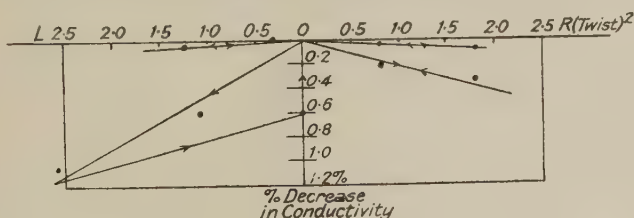


FIG. 1.—HARD ALUMINIUM.

The upper curve shows the decreases in the electrical conductivity, and the lower curve those in the thermal conductivity of a hard aluminium wire, plotted against the square of the twist which is measured in degrees per cm.

against the coils and slide wire of the same Callendar-Griffiths Bridge, placed in another circuit. The sensitivity was such that a change in the resistance of one part in 10,000 was equivalent to 0.3 mm. on the galvanometer scale. The mean of a

large number of readings both with direct and reversed current was taken, and the usual accuracy attained was one in 10,000, in a resistance of about 0.001 ohm, which was not found absolutely. A twisted hard wire was compared with a hard wire, a crystal with a crystal, and so on.

In the following tables, typical results are shown, with values of the twist in degrees per cm., and of the square of the twist. The resistance of the case coil is shown for each reading. 1°C. is equivalent to 0.0070 ohm.

VII. TABLES OF RESULTS.

(1) Hard aluminium wire. Diameter=2.00 mm.
Current=0.330 amp. ; $x_0=5.6$ cms. ; $x_B=4.7$ cms. ; $x_A=1.8$ cms.
Value of K from equation (4)=0.495.

Thermal Conductivity.

Date.	Case Coil (ohms).	Twist ° per cm.	(Twist) ² .	Conductivity.	Per cent. Change.
20/4/25	2.5002	0	0	1.0000	...
	2.5019	0.89R	0.79	0.9978	-0.22
	2.5016	1.34R	1.79	0.9964	-0.36
22/4/25	2.5092	0	0	1.0000	...
12/5/25	2.5302	0	0	1.0000	...
	2.5297	1.07L	1.14	0.9940	-0.60
	2.5285	1.60L	2.56	0.9895	-1.05
14/5/25	2.5312	0	0	0.9940	-0.60
15/5/25	2.5330	0	0	1.0000	...
<i>Electrical Conductivity.</i>					
1/10/25	...	0	0	1.0000	...
	...	0.89R	0.79	0.9998	-0.02
	...	1.34R	1.79	0.9991	-0.09
	...	0	0	1.0000	...
	...	0.54L	0.29	1.0000	-0.00
	...	1.10L	1.21	0.9994	-0.06
	...	0	0	1.0000	...

(2) Single crystal. Diameter=1.92 mm.
Heating current=0.330 amp. ; $x_0=4.8$ cms. ; $x_B=4.05$ cms. ; $x_A=1.05$ cms.
 $K=0.496$.

Thermal Conductivity.

Date.	Case Coil (ohms).	Twist ° per cm.	(Twist) ² .	Conductivity.	Per cent. Change.
17/2/25	2.5589	0	0	1.0000	...
	2.5581	1.04R	1.08	1.0000	...
	2.5607	0	0	0.9985	-0.15
19/2/25	2.5572	0	0	1.0000	...
	2.5563	1.04L	1.08	1.0015	+0.15
	2.5579	0	0	0.9985	-0.15
<i>Electrical Conductivity.</i>					
3/11/25	...	0	0	1.0000	...
	...	0.58R	0.34	0.9998	-0.02
	...	0.87R	0.76	0.9995	-0.05
5/11/25	...	0	0	1.0000	...
	...	0.58L	0.34	0.9998	-0.02
	...	0.87L	0.76	0.9993(5)	-0.06(5)
	...	0	0	1.0000	...

The Effects of Torsion on Conductivity.

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(3) Annealed wire. Diameter = 2.00 mm.

Heating = current 0.330 amp. ; $x_G = 5.9$ cms. ; $x_B = 5.0$ cms. ; $x_A = 2.0$ cms.

$K = 0.490$.

Thermal Conductivity.

Date.	Case Coil (ohms).	Twist ° per cm.	(Twist) ² .	Conductivity.	Per cent. Change.
4/6/25	2.5537	0	0	1.0000	...
	2.5548	0.85R	0.72	1.0010	+0.10
	2.5560	1.29R	1.66	1.0005	+0.05
	2.5541	0	0	1.0005	+0.05
10/11/25	...	Electrical	Conductivity.		
	...	0	0	1.0000	...
	...	0.57R	0.33	0.9998	-0.02
	...	0.90R	0.81	0.9994	-0.06
	...	0	0	1.0000	...
	...	0.57L	0.33	0.9998	-0.02
	...	0.90L	0.81	0.9994	-0.06
	...	0	0	1.0000	...

(4) Few crystals. Diameter = 1.95 mm.

Heating = current 0.330 amp. ; $x_G = 5.6$ cms. ; $x_B = 4.7$ cms. ; $x_A = 2.0$ cms.

$K = 0.490$.

Thermal Conductivity.

Date.	Case Coil (ohms).	Twist ° per cm.	(Twist) ² .	Conductivity.	Per cent. Change.
18/6/25	2.5343	0	0	1.0000	...
	2.5337	0.90R	0.81	0.9990	-0.1
	2.5337	0	0	0.9995	-0.05
19/11/25	...	Electrical	Conductivity.		
	...	0	0	1.0000	...
	...	0.61R	0.37	0.9998	-0.02
	...	0.97R	0.94	0.9995	-0.05
	...	0	0	1.0000	...
	...	0.61L	0.37	0.9998	-0.02
	...	0.97L	0.94	0.9994	-0.04
	...	0	0	1.0000	...

These results are exhibited graphically in Figures 1 and 2.

VIII. DISCUSSION OF THE RESULTS.

In the tables given above it is to be remembered that the accuracy for the single crystal is 0.15 per cent., while for the hard, the unannealed and the wire consisting of a few crystals the accuracy in the thermal measurements is 0.1 per cent. These and similar results appear to show no change in a crystal wire greater than 0.1 per cent. in the thermal conductivity, though the hard wire gave decreases greater than this, in very reasonable agreement with the earlier results for an aluminium wire. On the other hand, the decreases in the electrical conductivities of the order of a few parts in 10,000 appear to be very much the same for the aluminium in all forms. The harder wire suffers a slightly smaller change than the softer forms, as Fig. 2

will show. Values for right and left twists have been plotted for the hard wire, while the values for the other wires are for right twists only, in order to save confusion.

Another point of interest is that there do not appear to be very large differences between the conductivities of the various wires.

Our values for the thermal conductivities were :—

Crystal A	0.496 C.G.S. units.
Crystal B	0.501 "
Hard Wire	0.495 "
Annealed Wire	0.490 "
Few Crystals	0.495 "

Agreement is more exactly tested for the electrical conductivities, which, however, were not measured absolutely. The ratio of the resistance of a hard wire

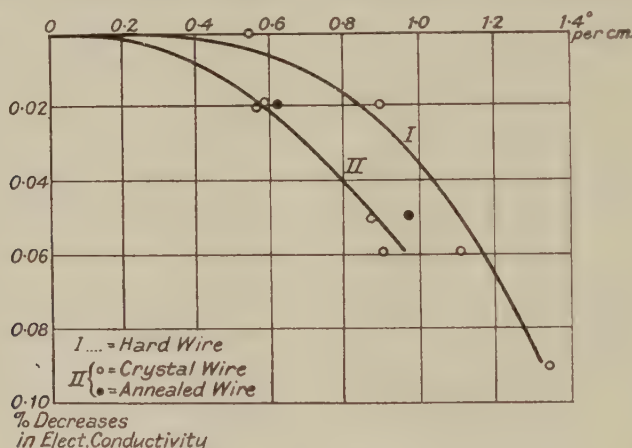


FIG. 2.—DECREASES IN ELECTRICAL CONDUCTIVITY.

The upper curve shows the decreases in the electrical conductivity of a hard aluminium wire, plotted against the twist, which is measured in degrees per cm. The lower curve shows the decreases for crystal and annealed wires. The black dots are for a wire consisting of a few crystals.

to that of a crystal from the comparison of both with the same crystal, and with correction for dimensions, was 1.0030.

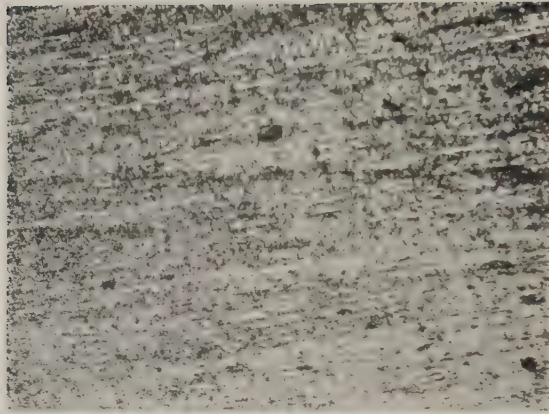
The above changes do not appear to be explained by the change in dimensions, as a change of 1 part in 40,000 for the twists used could not be detected. This was the limit of accuracy obtainable. Poynting's* results for steel and copper would lead us to expect a longitudinal extension and a lateral contraction of the order of 1 in 1,000,000.

It would appear that in the process of drawing the crystals may become elongated or thread-like. Work by X-ray methods shows that the [111] direction of the crystal lattice lies parallel to the direction of drawing.

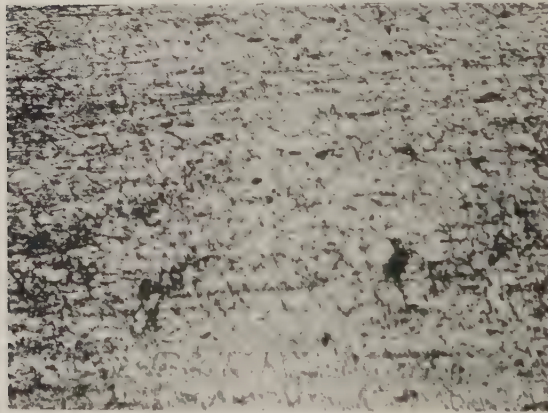
Eltisch and Polyani† found, in addition to the [111] direction, a smaller number

* Collected papers, p. 397.

† Zeits f. Phys., 7, pp. 181-184 (1921); Zeits f. Phys. Chem., 99, pp., 332-337 (1921).



ALUMINIUM WIRE AS DRAWN $\times 100$.



ALUMINIUM WIRE ANNEALED $\times 100$.



PORTION OF SINGLE ALUMINIUM CRYSTAL $\times 100$.

of crystals with [100] parallel to this direction, which effect was not very prominent in the later work of Sachs and Schiebold.*

I suggest that the larger changes in the thermal conductivity of the hard wire are because of this structure.

If the crystals are to follow the shear of the wire, they must be extended while undergoing lateral pressure. The density of the hard wire was 0.2 per cent. greater than that of a crystal wire, so that the changes found appear to be consistent with Bridgman's results, mentioned earlier in the Paper.

Annealing renders the crystals of more uniform size in all directions, as may be seen from the second photograph, and in this state the crystals would more easily follow the shear of the wire.

It is presumed that the changes in a crystal are small because the body is very isotropic. It is possible that some such lattice theory as J. J. Thomson's† might predict such changes from the distortion of the space-lattice, but Bridgman's‡ results for pressure on some non-cubic metal crystals lead him to believe that resistance is determined by the details of the atomic structure, and not merely by the distance apart of the atoms. Some idea of the differences in structure of the various specimens may be gathered from the micro-photographs, for which I am indebted to the kindness of a former pupil, Mr. E. Musgrave.

In conclusion, I should like to tender my sincere thanks to Prof. H. C. H. Carpenter and Miss C. F. Elam for providing the materials for this work, and to Prof. C. H. Lees, in whose laboratory the experiments have been made.

DISCUSSION.

Prof. O. W. RICHARDSON complimented the author on a very careful piece of work. He thought it remarkable that the thermal conductivity effect should be absent in the case of single crystals.

Miss C. F. ELAM said that it had given great pleasure to Prof. Carpenter and herself to furnish the author with single crystals, as they found it impossible to investigate all the properties of these themselves and were much interested in the results obtained by others. In finding the electrical conductivity of drawn metal less than that of single crystals the author was in agreement with previous results, but his relative values for the densities appeared to be inconsistent with the usual experience, which is that the drawn metal is less dense than the annealed. She did not think that the differences in conductivity between the various forms of the metal are mainly attributable to changes in the orientation of the crystals, for other physical properties are much affected when the metal is very slightly worked, while definite changes in orientation do not affect the physical properties to a corresponding extent.

Dr. E. H. RAYNER said that he noticed that the aluminium used contained 0.2 per cent. each of silicon and iron, both of which have a marked effect on electrical conductivity. It seemed doubtful whether such a small proportion of impurity can have a serious effect on the structure of a single crystal, yet it has been found that the addition of 0.4 per cent. of Si will alter the resistance of aluminium by 2 or 4 per cent. It has also been found that if the aluminium be treated with an alkali metal the Si loses its effect.

Mr. ROLLO APPELVARD asked how far different specimens of the same kind differed from one another in density.

The Author, in reply, said that he did not insist on his suggestion that the effect of stress on conductivity is to be explained by distortion of the space lattice, but it might be anticipated that any changes due to such a cause would be small, since Bridgman has found that the resistances measured along different axes of non-cubic crystals differ by only 30 per cent. All the specimens examined were taken from the same stock of original material.

* *Naturwissenschaften*, p. 964, Nov. (1925).

† *Phil. Mag.*, 44, p. 657 (1922).

‡ *Proc. N.A.S.*, 10, pp. 411-415 (1924).

XXV.—A STUDY OF THE CONCURRENT VARIATIONS IN THE THERMIONIC AND PHOTO-ELECTRIC EMISSION FROM PLATINUM AND TUNGSTEN WITH THE STATE OF THE SURFACES OF THESE METALS.

By T. H. HARRISON, *B.Sc.*, King's College, London.

ABSTRACT.

An attempt has been made to measure the thermionic and photo-electric work functions for the same specimens of tungsten and platinum. It is found that in all cases the results depend greatly on the previous heat treatment of the material. In the case of platinum the curves showing the dependence of photo-electric sensibility on the wavelength of the irradiation are of four different types, while as regards thermionic properties the specimens can take up either a "large-emission" or a "small-emission" state, according to their treatment. The photo-electric work function of platinum appears to be greater than the thermionic, but no definite results were obtained for tungsten. The photo-electric curves obtained for both metals did not end abruptly so as to indicate a maximum wavelength for emission, but extended asymptotically towards zero emission in the direction of increasing wavelength. These irregularities in behaviour are attributed by the author to the state of the surface of the specimens.

INTRODUCTION.

THE photo-electric and thermionic work functions of tungsten and of platinum are known to be of the same order of magnitude under certain circumstances, and it is desirable to determine whether they are really equal. No measurements of both quantities have been made for the same specimen of either metal, and the differences known to exist between the work functions for different specimens make it impossible, from the available data, to establish or disprove the identity of the two work functions. The work described in what follows is an attempt, made at the suggestion of Prof. O. W. Richardson, to measure both quantities for the same samples of the two metals above mentioned.

EXPERIMENTAL METHOD.

Two specimens of tungsten and two of platinum were used for the work. These were enclosed in tubes which, in the case of the tungsten specimens, took the form shown in Fig. 1. In the first tube the tungsten was in the form of a plane spiral filament 12 cm. long and 0.23 mm. in diameter, while in the second (shown in the figure) a cylindrical spiral filament was used, so as to intercept more radiation.

In the case of platinum, a strip 10 cm. long, 1.5 mm. wide and 0.02 mm. thick was stretched vertically along the axis of a copper cylinder also 10 cm. long, which served as the anode, and which had suitable holes made half way along its length to form an entrance and an exit for the ultra-violet radiation. Two specimens of this metal too, were used in the work.

The vacuum was obtained by means of a Gaede rotary mercury pump, backed by a Geryk pump, and the pressures were measured by a McLeod gauge. Between the McLeod gauge and the photo-electric thermionic tube were a coconut charcoal tube and a mercury vapour trap, both of which could be immersed in liquid air. Without the use of liquid air a pressure of 10^{-4} mm. of mercury was obtainable, and in the latter experiments of 2×10^{-5} mm. With the aid of liquid air pressures com-

pletely immeasurable could be obtained, although when the filaments or strips were heated the pressure would rise to about 10^{-5} mm. unless the metal had previously been well "glowed out."

For the photo-electric measurements, a quartz mercury vapour lamp was used, the radiation of which was passed through a Hilger monochromatic illuminator. The telescope tube (the slit and eyepiece being removed) was fitted over the end of one of the tubes above described, the ultra-violet radiation passing through the quartz window, and the image of the collimator slit being formed at a slit inside the photo-electric tube from which the radiation diverged on to the tungsten spiral, or, in the case of platinum at the central portion of the platinum strip itself. The relative values of the energy in the various wavelength regions were assumed to be the same as those found by Compton and Richardson for similar apparatus.*

For the thermionic measurements, the tungsten spiral or the platinum strip was heated by passing an electric current through it which was measured by an ammeter, the resistance being simultaneously measured with a Wheatstone bridge.

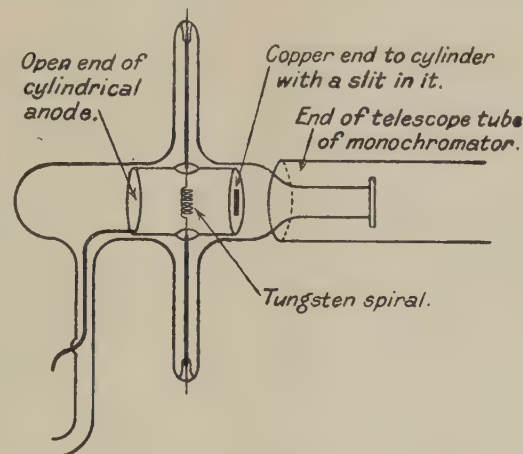


FIG. 1.—DIAGRAM OF THE SECOND TUNGSTEN TUBE:

The photo-electric currents were measured with a quadrant electrometer with a sensitivity of 650 mm. per volt per metre scale distance.

The thermionic currents were measured for tungsten with a micro-ammeter with shunts and for platinum by a galvanometer with suitable shunts.

The photo-electric currents for different wavelengths in the mercury vapour lamp spectrum were measured and the photo-electric sensitivity curves were drawn. From these the long wave limit could be estimated.

For obtaining the thermionic work function, use was made of Prof. Richardson's formula $i = AT^{1/2}e^{-\phi/kT}$, or $\log_{10} i - \frac{1}{2} \log_{10} T = \log_{10} A - (\phi/2.303k)T^{-1}$. Plotting the experimentally found values of $\log_{10} i - \frac{1}{2} \log_{10} T$ as a function of $1/T$, the curve should be, providing the nature of the surface does not change, a straight line, the inclination of which gives the work function ϕ .

* Compton and Richardson, Phil. Mag., 26, p. 549.

EXPERIMENTAL RESULTS FOR THE FIRST TUNGSTEN SPECIMEN.

(a) *Photo-Electric.*

For some time after the first tube had been baked and glowed, any photo-electric currents produced by light passing through the monochromator were too small to measure. After a further glowing of the tungsten filament, however, the sensitivity was increased, and a large number of sets of readings were taken over a considerable period, some at comparatively high pressures of 2 or 3×10^{-4} mm. of mercury without the use of liquid air, and others, with the use of liquid air, at pressures almost immeasurable on the McLeod gauge. Some of the later sets of readings were taken, after a further glowing of the filament, at a temperature of about $2,300^{\circ}\text{K}$. For several hours after this glowing the photo-electric currents did not re-appear, but after two or three days, the pressure never rising above 10^{-4} mm., readings almost identical with the previous ones were obtained. A typical set of readings is given in Table I below. It is to be noted that with an anode potential of 50 volts the photo-electric currents were no greater than with one of 2 or 3 volts.

TABLE I.—*Typical Set of Readings of Photo-Electric Current for the First Tungsten Tube.*
 $p = 10^{-6}$ mm. Slit of monochromator 0.05 in. wide. Anode volts = 7.

λ in Å.U.	2,540	2,530	2,520	2,550	2,766	2,820	2,766	2,820	2,766	2,820	2,766	2,820
Deflection of electro- meter in 5 mins. less dark current ...	15.2	16.3	13.5	17.1	2.0	1.6	2.0	1.8	2.0	1.9	2.2	1.7
λ in Å.U.	2,766	2,820	3,020	2,662	2,545	2,480	2,377	2,343	2,260	2,300	2,450	2,300
Deflection in 5 mins....	1.7	1.5	0.8	5.1	14.7	5.5	4.9	3.6	3.0	3.7	3.1	4.4

Dividing the photo-electric currents by the energy of the light beam at the corresponding wavelength, the sensitivity curve for tungsten is obtained. This is shown in Fig. 2. It must be borne in mind, however, that these photo-electric currents being extremely small, the accuracy cannot be great, and also that the relative energies in various parts of the spectrum of the mercury vapour lamp and monochromator combination used in these experiments may not be absolutely identical with those found by Compton and Richardson with similar apparatus. Nevertheless, for the purposes of this Paper, it will be sufficient to assume the identity of the two energy distributions.

The main point of interest in Fig. 2 is that the main part of the curve approaches the wavelength axis as if it would cut it at about 2,700 Å.U., but, instead of doing this, it bends round and finally approaches it so gradually as to make it appear asymptotic. This "asymptotic" extension of the photo-electric sensitivity curve appears in almost all the photo-electric experiments.

Later results on platinum show that only an insignificant part of this "foot" is due to stray light from the monochromator, hence it must be concluded that this "foot" is real, although its cause is obscure.

Neglecting the "foot," the long wave limit is at about 2,700 Å.U., otherwise it must be greater than 3,000 Å.U.

b) Thermionic.

In the case of the tungsten specimens the temperature was estimated by two methods:—

- (a) By the increase of resistance of the filament ;
- (b) By the heating current, together with the known diameter of the filament.

The temperature required is that of the central portion of the filament, since the cooler ends emit relatively few electrons. Data regarding the allowance to be made for the cooler ends of the filament in estimating the temperature by the change

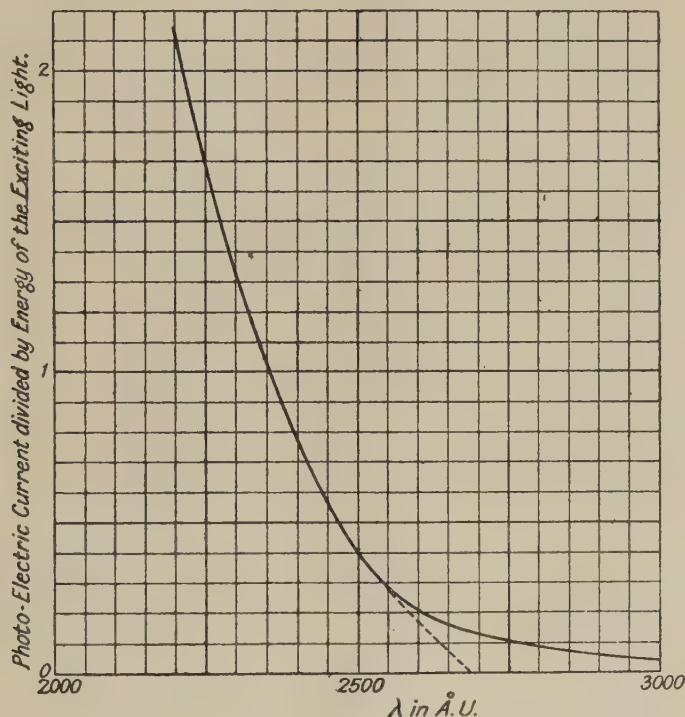


FIG. 2.—SENSITIVITY CURVE IN THE FIRST TUNGSTEN TUBE.

in resistance of the filament, and also the relationship between the heating current and the diameter of the filament and its temperature were obtained from a Paper by Stead.* The temperatures as estimated from the heating current are about 30° higher than those estimated from the change of resistance.

Notwithstanding a considerable amount of baking out of the tube and glowing the filament, a state was never reached in which no gas was evolved when the filament was first switched on ; nevertheless, after a short time the liquid air and charcoal would reduce the pressure to between 5×10^{-5} and 10^{-6} mm. Possibly better conditions might have been obtained eventually, but for the premature

* Stead, *Journal of Inst. of Elec. Engrs.*, 58, p. 107 (1920).

collapse of the tube in baking it out. Five sets of readings were taken, all at pressures between 10^{-5} and 10^{-6} mm., two sets with decreasing temperature and three with increasing temperature. The curves for $\log_{10} i - \frac{1}{2} \log_{10} T$ as a function of $1/T$, when T is estimated from the resistance, are shown in Fig. 3. With the exception of

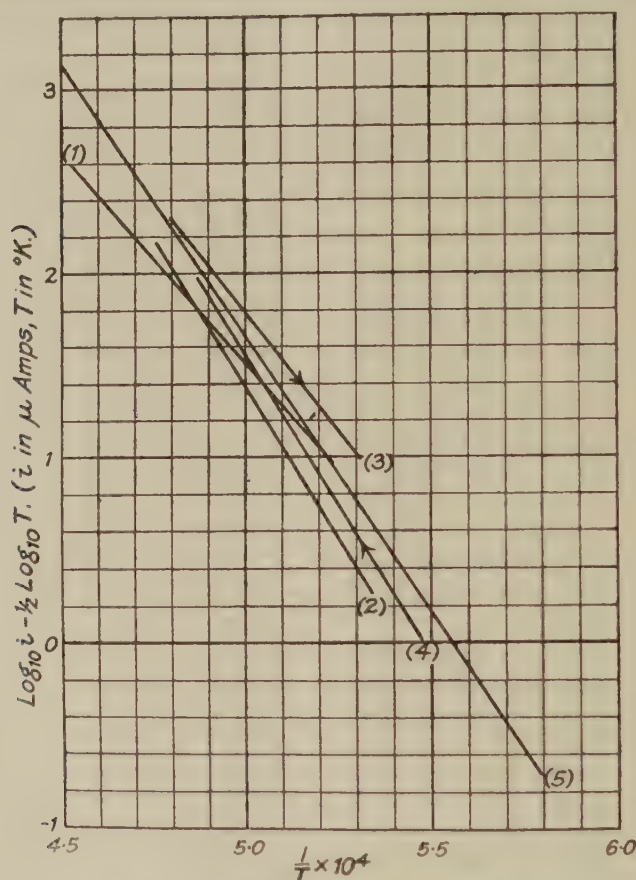


FIG. 3.—THERMIONIC CURVES OF TUNGSTEN.

the readings in Set 3, the points are found to lie very close to straight lines, and the values of ϕ as calculated from the inclination of these straight lines are given below :—

Temperatures estimated from heating current	{	Set 1 Falling temperature.	$\phi = 4.64$ volts	(about)
		" 2 Rising "	$\phi = 6.32$ "	
		" 3 Falling "	$\phi = 4.8$ "	
		" 4 Rising "	$\phi = 5.97$ "	
		" 5 Rising "	$\phi = 6.65$ "	
Temperatures estimated from change of resistance.	{	Set 1 Falling temperature.	$\phi = 4.78$ volts.	(about)
		" 2 Rising "	$\phi = 6.52$ "	
		" 3 Falling "	$\phi = 5.0$ "	
		" 4 Rising "	$\phi = 6.57$ "	
		" 5 Rising "	$\phi = 6.00$ "	

As the temperature of the filament was increased, a certain amount of gas was evolved since the pressure would rise from about 10^{-6} mm. to about 5×10^{-5} mm. After a few minutes, however, the charcoal would absorb this gas, and the pressure again be almost immeasurably low, until the temperature of the filament was again increased. Thus, it appears likely that the difference between the work functions observed for rising temperature and for falling temperature is due to the presence of gas which apparently causes the work function to be higher while it is being evolved.

The value of the work function for falling temperatures is about 4.8 volts, and this agrees with that found by Davisson and Germer.* The long wave limit corresponding to 4.8 volts is 2,570 Å.U.

EXPERIMENTAL RESULTS FOR THE SECOND TUNGSTEN SPECIMEN.

As stated before, the second tungsten filament intercepted more light than the first. Further, the Gaede pump was improved and higher vacua obtained.

Before any measurements were made, the tube was baked out at 350°C . and the spiral heated to about $2,400^{\circ}\text{C}$. Upon attempting to make photo-electric measurements it was found that instead of having larger photo-electric currents than those previously obtained, as was expected, no measurable currents at all were produced by light passing through the monochromator. After 48 hours, however, the following extremely small photo-electric currents were measured.

TABLE II.
 $p = 10^{-4}$ mm. Liquid air on trap, but not on charcoal.

λ in Å.U.	Anode volts = 7.5		Anode volts = 100.				
	2,540	2,540	2,540	2,480	2,450	2,378	2,260
Deflection of electrometer in 5 mins., less "dark current"	2.2	1.9	1.8	0.6	0.3	0	0.4

The "dark current" for the above set of readings gave a deflection of -0.8 cm. in 5 minutes when the anode potential was 100 volts, and $+0.7$ cm. when the anode potential was only 7.5 volts. These "dark currents" were measured several times with satisfactory agreement.

The tube was then rebaked several times to 350°C . for periods up to 15 hours, and the filament was again glowed, the pressure being reduced to 5×10^{-5} mm. without the use of charcoal. Then using liquid air on the charcoal, the pressure was reduced below the measuring capacity of the gauge. No photo-electric currents were measurable until after two or three days after the glowing of the filament. The set of readings given in Table III shows the exceedingly small currents which were then obtained.

TABLE III.
 p not measurable. Anode volts = 7.5.

λ in Å.U.	2,540	2,380	2,260	2,054	1,975	1,943	1,850	Full light of lamp. No monochromator.				Glass screen.	Quartz screen
Deflection in 1 min.	0.4	1.2	1.1	0	0	0	0	21.4	23.8	23.6	30.0	-0.1	5
Deflection in 5 mins.	0.2	0.9	0.9	0	0	0	0	0	28.4

* Davisson and Germer, Phys. Rev., 20 (1922).

After another three days without heating the filament, the sensitivity increased to the values shown in Table IV.

TABLE IV.

 $p = 10^{-6}$ mm.

Anode volts = 7.5.

Nature of illumination.	2 cm. water screen.	Water screen.	Glass screen.	Full light.	Full light.	2 mm. quartz screen.	Quartz screen.	2 cm. methyl alcohol.	Methyl alcohol screen.
Deflection in 1 min.	8.4	7.9	-0.1	170	170	40	40	11.4	12.5
Deflection in 5 mins.	25.9	25.9	0	34.4	...
Nature of illumination.	Glass screen.	Full light.	Å.	Å.	Å.	Å.	Å.	Glass screen.	...
			2,537	2,652	2,470	2,450	2,378		...
Deflection in 1 min.	-0.3	180	0.7	0.6	-0.3	0	0.6	0.5	...
Deflection in 5 mins.	0.0	...	1.9	0.9	+0.1	0.3	1.2	0.5	...

Several further attempts were made at various pressures to obtain larger photo-electric currents but without success. In one of the sets of readings without the use of the monochromator, taken soon after a glowing of the filament, the 2 mm. thick fused quartz screen was found to cut down the photo-electric current to about one-thirtieth of its previous value. On lowering the liquid air flask for a fraction of a second from the trap, the photo-electric currents were increased to the values shown in Table IV, without any rise of pressure being recorded by the McLeod gauge, but on removing the liquid air from the charcoal tube, no further increase in photo-electric sensitivity took place, although the pressure gradually rose from below 10^{-6} mm. to 5×10^{-2} mm.

It is thus seen that the long wave limit for tungsten is distinctly variable. The effect of glowing the tungsten to about $2,400^\circ\text{K.}$ is to increase the photo-electric work function. With lapse of time, however, the work function again becomes smaller, but this decrease in work function can be made to occur almost instantaneously by lowering the liquid air from the trap for a fraction of a second. When the tungsten has not been recently glowd, the long-wave limit is certainly higher than 2,650 Å.—i.e., its photo-electric work function is less than 4.6 volts. About two or three hours after glowing the tungsten the wavelength limit would appear to be in about the same region as that found by Hagenow*—namely, at about 2,300 Å., with a work function of about 5.36 volts. In all cases, the photo-electric sensitivity curves seem to tail off as the wavelength is increased, the photo-electric currents in the "tail" being too small to ascertain whether there is a definite end to it.

GENERAL CONCLUSIONS FOR TUNGSTEN.

Although photo-electric and thermionic measurements have been made upon the same sample of tungsten, it is found that very small changes in the previous history affect both work functions considerably. It follows that the tungsten was probably in a different state for the photo-electric measurements and for the thermionic measurements. Until the thermionic and photo-electric work functions can

* Hagenow, Phys. Rev., 13, p. 415 (1919).

measured whilst the metal is in the same state, there can be no proof of their identity, but, on the other hand, there is nothing in the above results which renders such an identity improbable.

EXPERIMENTAL RESULTS FOR THE FIRST PLATINUM SPECIMEN.

Photo-Electric.

Owing to the disappointing nature of the results obtained with tungsten, it was decided to carry out similar measurements on platinum in the hope that more positive information might be obtained.

Two samples were used, as described in the first section of the Paper. A large number of photo-electric readings with the first strip were taken before any ther-

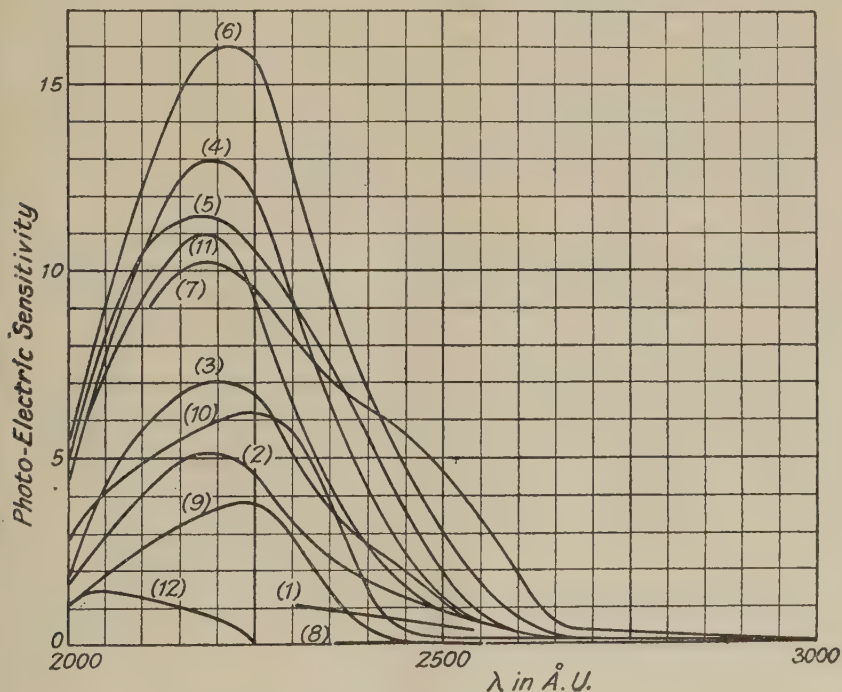


FIG. 4.—PHOTO-ELECTRIC SENSITIVITY CURVES FOR SECOND SAMPLE OF PLATINUM.

ionic readings were taken at all. The sensitivity curves showing the photo-electric currents per unit energy of monochromatic light at various wavelengths could be divided into five types. These are not shown, owing to lack of space, but similar ones are shown in Fig. 4 for the second sample of platinum.

Type 1 occurred several hours after a glowing of the platinum to a reddish yellow heat, and also after a further glowing at a brighter yellow heat, the pressure during the photo-electric readings being below the least measurable value. The shape of the curve was similar to that of curve 2, Fig. 4, but the average sensitivity was only half as big, whilst the "foot" of the curve was longer, showing a long wave limit of 2,900 Å.

Type 2 was found an hour or two after glowing to a brighter yellow heat, and was almost identical with curve 2, Fig. 4, showing a long-wave limit of 2,660 Å.

Type 3, found two or three days after Type 2, without any intervening heat treatment, and with the pressure kept below the measurable limit for the whole time, had the same shape as Type 1, with an increase in sensitivity of about 50 per cent. for all wavelengths, the long wave limit being at 2,900 Å.

Type 4, found an hour or two after glowing the platinum for seven hours at about 1,425°C., with a pressure of 5×10^{-6} mm., was of the same shape as curve 4, Fig. 4, the sensitivity at all wavelengths being 0.8 times as large. The long-wave limit was at 2,660 Å.

Type 5, found 24 hours after Type 4, the low-pressure being maintained and no heat treatment being given in the meantime, showed a very large increase in the sensitivities for wavelengths between 2,500 Å. and 3,000 Å., besides a small increase for the shorter wavelengths. It corresponded to curve 7, Fig. 4, but extended very much further towards longer wavelengths, the long wave limit being 3,000 Å. At 2,800 Å. the sensitivity was 1.0 on the same scale as Fig. 4, whilst the maximum sensitivity at 2,250 Å. was 11.5. In all of these types there was a maximum sensitivity at about $\lambda = 2,200$ Å.

The nature of these five typical sensitivity curves depended upon the previous heat treatment of the strip and the interval of time since that treatment.

In no case that was investigated with the first strip was there any evidence of a definite long wavelength limit, the currents dying down gradually with increasing wavelength until they became too small to detect. There was, however, in most of the curves a more or less defined region where the curve, instead of continuing to meet the wavelength axis, bent round and proceeded at a small inclination to it, as if the final approach might be asymptotic. Part of this "foot" was doubtless due to stray light of shorter wavelengths, scattered by the monochromator, and some attempt was made to discover to what extent this was the case by using as a filter a solution of cobalt and aluminium chlorides. The solution absorbed too much light, however, and the attempts were discontinued, since further sensitivity curves threw some light on the subject, and showed that at any rate a considerable fraction of the currents in the "foot" was due to the monochromatic light of wavelength indicated on the drum of the monochromator. When, for example the third and fourth types of sensitivity curves for the first platinum strip were compared, it was seen that at $\lambda = 2,700$ Å.U. the apparent sensitivity for Type 3 was about four times that for Type 4, and yet the stray light of short wavelengths in Type 4 must have been twice as effective as that for Type 3, the condition of the monochromator being the same in both cases. Thus, in Type 3 it is justifiable to say that at 2,700 Å.U. at least seven-eighths of the ordinate is due to radiation of $\lambda = 2,700$ Å.U., but that the remaining one-eighth may be due to stray radiation. It thus appears that the greater part of the "foot" of the sensitivity curves is real, and not due to stray light. On the other hand, it is not justifiable to say that the wavelength axis is asymptotic to the curve, since there are no means of measuring the exceedingly small photoelectric currents for the longer wavelengths, and since the spurious "stray light" currents may become relatively larger as the wavelength increases.

In the absence of any definite "long-wave limit" the sensitivity curves have been prolonged to meet the axis by dotted lines from the points at which the "foot" begins, and the wavelength at the intersection of these dotted lines and the axis will be referred to as the "long-wave limit."

Comparing the five typical curves found for the first strip, in all of which the anode was maintained at 7.5 volts, or more than sufficient to promote saturation, it is found that the immediate effect of heating the strip is to increase the sensitivity for the shorter wavelengths, and decrease it for the longer wavelengths, but, with lapse of time, the after effect of this heat treatment is an all-round increase in sensitivity, notwithstanding the fact that the pressure has by the use of charcoal and liquid air been kept too low to be measured by the McLeod gauge. The effect of heating the platinum to white heat $1,425^{\circ}\text{C}.$, is of the same kind as that of heating it only to yellow heat, but is more pronounced. Before the $1,425^{\circ}\text{C}.$ glowing the "long wave-limit" is at $2,900 \text{ \AA.U.}$, while an hour afterwards the limit is at $2,660 \text{ \AA.U.}$ After 24 hours, however, the pressure being very low the whole time, λ_0 is at $3,000 \text{ \AA.U.}$, and the sensitivity is very high.*

(b) *Thermionic.*

The temperatures of the strip were measured by its resistance, this being measured in arbitrary units corresponding to the addition of 1 ohm in the variable part of a Post Office box. The "end-effects" were allowed for in the temperature estimations, a subsidiary experiment being carried out with two thermionic tubes, each with a strip of platinum of the same breadth and thickness, but of different lengths.

Having applied the corrections for the effects of the leads and end cooling found by this subsidiary experiment, the temperatures of the strip can be calculated from the known resistivity-temperature curve of platinum.

Six sets of thermionic readings were taken, and the graphs of $\log_{10} i - \frac{1}{2} \log_{10} T$ were plotted as a function of $1/T$. These graphs were similar to those shown in Figs. 5 and 6, i being measured in units of about 10^{-9} amps. by a galvanometer, and T being measured in $^{\circ}\text{K}.$ It was noticed that, until the platinum had been heated for a long time at a pressure as low as possible with liquid air and charcoal, the thermionic currents were large, but after a time they quickly decreased to about one-thousandth part of their previous value. For this reason, it is convenient to call the state in which the larger thermionic currents are obtained "The Large Emission State" and the other "The Small Emission State."

The values of work functions are given in Table V:—

TABLE V.

	Large Emission State.			Small Emission State.		
	Set 1.	Set 2.	Set 3.	Set 4.	Set 5.	Set 6.
Pressure	10^{-4}	10^{-6}	10^{-4}	10^{-6}	5×10^{-6}	5×10^{-6}
ϕ in volts	3.77	4.33	3.97	4.09	3.52	4.23
Corresponding λ_0 ...	3,275	2,850	3,110	3,010	3,500	2,920

* It is worthy of note that at the commencement of the glowing at $1,425^{\circ}\text{C}.$, which preceded the measurements shown in Curve 4, the thermionic current density was about one-quarter of that for tungsten at the same temperature—i.e., 30 micro-amperes for the whole strip—but after two hours it fell to about one-thousandth of this value, the pressure never being more than $5 \times 10^{-5} \text{ mm.}$, and during the latter part of the glowing not more than 10^{-5} mm. In taking the measurements which contribute to the fourth type it was noticed that there was a growth of sensitivity at the longer wavelengths with time, so that all the time the sensitivity curve was gradually approaching that of the fifth type.

At the highest temperature above those used in taking the readings of Set 1, the thermionic currents decreased quickly approaching the "small emission" state.

In Set 2 it is probable that the temperature estimations are too high owing to evaporation of the strip at temperatures approaching its melting point during the course of the previous set of readings of Set 4, and that in consequence the value of the work function is over estimated.

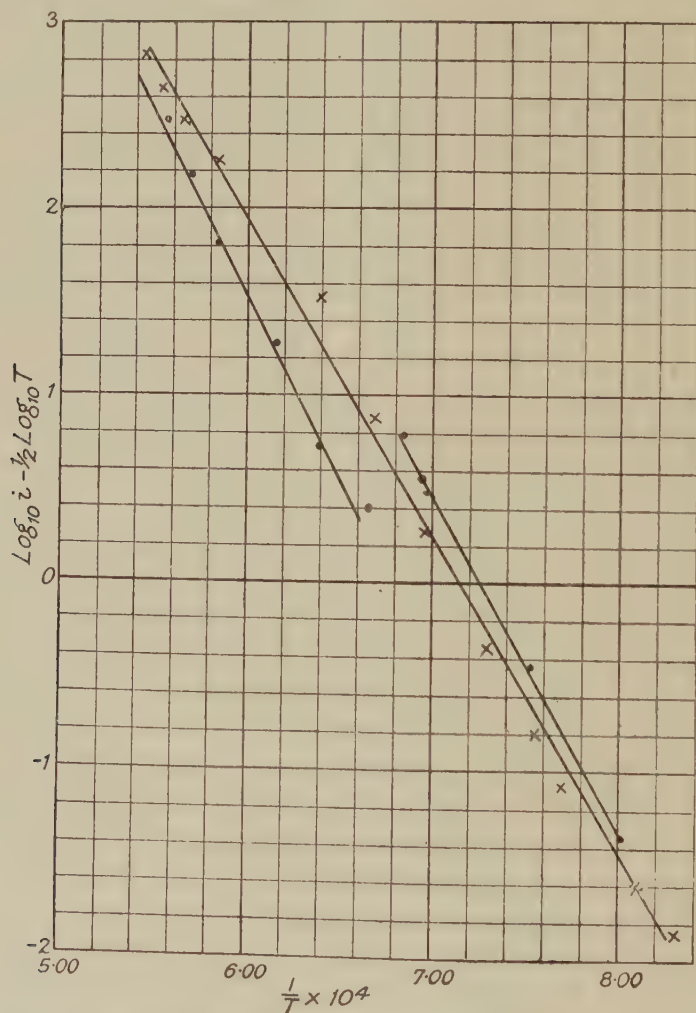


FIG. 5.—THERMIONIC CURVES FOR SECOND SAMPLE OF PLATINUM (Large Emission State).

In subsequent measurements this effect of the strip becoming thinner owing to evaporation of the platinum at high temperatures was allowed for in the following way: Knowing the temperatures in the earlier measurements as estimated from the resistance, and the heating currents corresponding to these temperatures, a curve connecting heating current and temperature was drawn, so that in the later

readings the temperatures could be estimated from the heating current as well as from the resistance. That estimated from the heating current is too low, while that estimated from the resistance is twice that amount too high. The deviations of the estimations from the true temperature were about 50° , showing the extent of the thinning of the strip through evaporation.

In some cases, measurements were made for both rising and falling temperature. Usually the curves found for rising temperature are rather steeper than

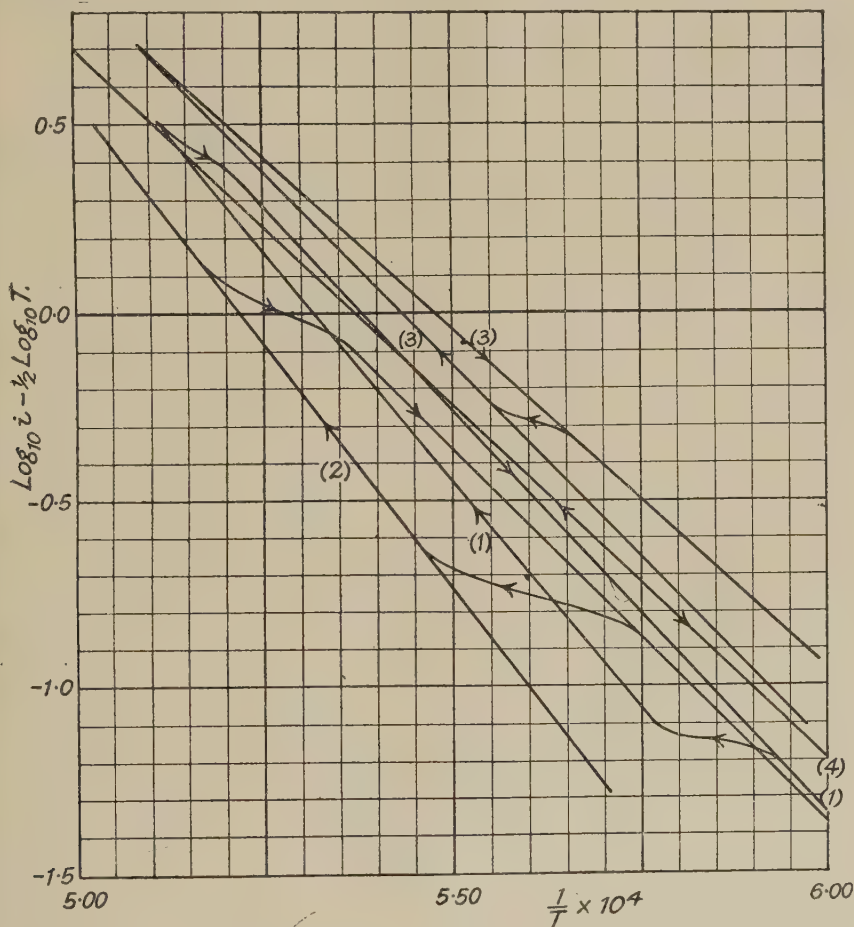


FIG. 6.—THERMIONIC CURVES FOR SECOND SAMPLE OF PLATINUM (Small Emission State).

those for falling temperature, the heating possibly altering the work function somewhat.

EXPERIMENTAL RESULTS FOR THE SECOND PLATINUM SPECIMEN

After the sixth set of readings with the first platinum strip it fused. The second strip was then placed in the same tube with the same leads, its breadth and thickness being the same as those of the first strip, but its length being 10.5 cm. instead of 10 cm.

The photo-electric sensitivity curves of the second strip are shown in Fig. 4. Details of these curves are :—

Curve 1— $p=10^{-6}$ mm., found $\frac{1}{2}$ hour after bright yellow hot glowing.

Curve 2— $p=10^{-6}$ mm., found $2\frac{1}{2}$ hours afterwards.

$$\lambda_0=2,650 \text{ \AA. } \phi=4.66 \text{ volts.}$$

Curve 3— $p=10^{-6}$ mm., found $4\frac{1}{2}$ hours afterwards.

$$\lambda_0=2,650 \text{ \AA. } \phi=4.66 \text{ volts.}$$

Curve 4— $p=10^{-6}$ mm., found about 1 hour after glowing to $1,600^\circ\text{C}$.

$$\lambda_0=2,650 \text{ \AA. } \phi=4.66 \text{ volts.}$$

Curve 5— $p=10^{-6}$ mm., found about 3 hours afterwards.

$$\lambda_0=2,650 \text{ \AA. } \phi=4.66 \text{ volts.}$$

Curve 6— p too low to measure, found a few hours after thermionic readings, during which a temperature of $1,700^\circ\text{C}$ was reached.

$$\lambda_0=2,650 \text{ \AA. } \phi=4.66 \text{ volts.}$$

Curve 7— p immeasurably low, found a few days after the aforementioned glowing.

$$\lambda_0=2,700 \text{ \AA. } \phi=4.57 \text{ volts.}$$

Curve 8— $p=2 \times 10^{-6}$ mm., found 2 or 3 minutes after a half-hour's glowing at $1,650^\circ\text{C}$.

Curve 9— $p=2 \times 10^{-6}$ mm., found a few minutes after Curve 8.

$$\lambda_0=2,450 \text{ \AA. } \phi=5.04 \text{ volts.}$$

Curve 10— $p=2 \times 10^{-6}$ mm., found about 1 hour after Curve 9.

$$\lambda_0=2,480 \text{ \AA. } \phi=4.98 \text{ volts.}$$

Curve 11— $p=10^{-6}$ mm., found 16 hours after Curve 10.

$$\lambda_0=2,600 \text{ \AA. } \phi=4.8 \text{ volts.}$$

Curve 12—Found $3\frac{1}{2}$ minutes after glowings at $1,700^\circ\text{C}$.

$$p \text{ immeasurably low. } \lambda_0=2,250 \text{ \AA. } \phi=5.48 \text{ volts.}$$

These curves are mostly of the same form as those for the previous strip, but no readings were taken after a dull yellow hot glowing and before the more severe heat treatment. Except for Curve 12, there is no evidence that there is a definite "long wave limit," and again it is noticed that stray light is not wholly responsible for the "foot" of the curves. The estimations of the long wave limit is as before, made by continuing the curves, by dotted lines from the point where the "foot" begins to cut the wavelength axis.

The thermionic curves of the second strip are shown in Figs. 5 and 6, those in Fig. 5 relating to the "large emission" state, and in Fig. 6 to the "small emission" state, these states being found for the second strip as well as for the first.

In Fig. 5, Set 1 (points marked \bullet) is in two parts, half an hour intervening between them. In both cases $p=10^{-4}$ mm., and the anode voltage=200.

For the lower temperature part $\phi=3.61$ volts, the corresponding $\lambda_0=3,420 \text{ \AA.}$

For the higher temperature part $\phi=4.07$ volts and $\lambda_0=3,030 \text{ \AA.}$

Set 2 (points marked X)— $p=10^{-4}$ mm. Anode volts=200.

$$\phi=3.42 \text{ volts. } \lambda_0=3,600 \text{ \AA.}$$

In Fig. 6—

Curve 1, with rising temperature— $p=2 \times 10^{-6}$ mm. Anode volts=200.

$\phi=4.88$ volts. $\lambda_0=2,530$ Å.

With falling temperature $\phi=4.27$. $\lambda_0=2,890$ Å.

Curve 2, with rising temperature— $p=2 \times 10^{-6}$ mm.

$\phi=5.17$ volts. $\lambda_0=2,390$ Å.

Falling temperature— $p=2 \times 10^{-6}$ mm.

$\phi=3.97$. $\lambda_0=3,110$ Å.

Curve 3— $p=2 \times 10^{-6}$ mm.

Rising temperature $\phi=4.08$ volts. $\lambda_0=3,020$ Å.

Falling temperature $\phi=3.62$ volts. $\lambda_0=3,410$ Å.

Curve 4—For both rising and falling temperature.

$\phi=3.76$ volts. $\lambda_0=3,280$ Å.

After the fifth photo-electric curve was taken, the first thermionic measurements, as shown in Curve 1, Fig. 5, were made. Following this, but under better vacuum conditions, Curve 1, Fig. 6, was taken, and after that Curve 2, Fig. 5, followed by Curve 2, Fig. 6.

After the severe heat treatment of the platinum during the course of these thermionic measurements, photo-electric Curve 6, Fig. 4, was found, from which it is seen that although this heat treatment has considerably increased the photo-electric sensitivity it has affected the "long-wave limit" very little. Notwithstanding the very high sensitivities at the shorter wavelengths, the "foot" of the curve lies very close to the axis showing that "stray light" currents at the longer wavelengths are quite small. The photo-electric Curve 7 was found a few days after Curve 6, the after-effect of the heat treatment being to increase the "long-wave limit," but to decrease the sensitivities at shorter wavelengths.

Hitherto no photo-electric measurements have been made until about an hour after the platinum has been heated. It is seen, however, that changes do occur with time after the heat treatment, so, in order to find the immediate effect of a white hot glowing of the platinum, it was heated to $1,670^\circ\text{C}$. in the course of a half-hour's glowing, and as soon as possible after switching off the heating current, photo-electric measurements were made. These are shown in Curve 8, Fig. 4, and it is noticed that for radiation of wavelength of $2,360$ Å.U. and above, there are no measurable photo-electric currents. It would therefore, appear that the large decrease in thermionic currents from the "large" to the "small emission" state in the course of prolonged heating to high temperature under the best vacuum conditions is accompanied by a large decrease in the photo-electric sensitivity. In the course of a few minutes, however, the sensitivity increases as witnessed by Curve 9, which was found a few minutes after Curve 8. This increase in photo-electric sensitivity and "long-wave limit" takes place under the very best vacuum conditions obtainable. At the same time the thermionic "small emission" state changes to the "large emission" state, but providing the vacuum is good only a very small amount of heat treatment is necessary to cause a reversion to the "small emission" state. About an hour after Curve 9, the measurements for Curve 10 were made, which shows an increase in sensitivity and in the "long-wave limit." Sixteen hours later, Curve 11 was found, showing a large increase in sensitivity with a corre-

spondingly large increase in the "long-wave limit." The thermionic readings for Curve 3, Fig. 6, were then made. The difference between the work functions for rising and falling temperatures is even more marked than in the case of the first strip, and it seems that, even with the best vacuum that could be obtained, the heating does alter the surface. After the first strip had fused, for example, the remnants of it were found to be pitted, and it is, therefore, not surprising that the work function should change somewhat. The strip was now heated nearly up to its melting point, and on switching off the heating current, the electrometer was connected up. The full light of the mercury vapour lamp gave an unmeasurably high photo-electric current with the electrometer, while a filter of $1\frac{1}{2}$ cm. of distilled water cut this current down so that it gave a deflection of 30 cm. in 5 seconds. Twelve hours later the sensitivity curve was almost identical with Curve 11. After another heating to about $1,700^{\circ}\text{C}$. more photo-electric measurements were made. For about 3 minutes after the heating current is switched off, there is a large but gradual decreasing non-photo-electric current, for which the previous large thermionic current is held to be responsible. This spurious current may be due to leakage from the glass walls of electrons which have been deposited there thermionically. In any case it certainly is not photo-electric, and it prevents photo-electric measurements, from being made until about $2\frac{1}{2}$ minutes after the heating current is switched off.

Photo-electric measurements after the above-mentioned heating to $1,700^{\circ}\text{C}$. showed at first no measurable current for $\lambda=2,360 \text{ \AA}$., but after ten minutes it had reappeared.

In order to obviate the difficulties due to an increasing sensitivity with time, a new type of set of photo-electric measurements was then made. The strip was heated for 10 minutes to about $1,650^{\circ}\text{C}$. before each photo-electric measurement, and then the deflections of the electrometer were measured every quarter of a minute, except during the first 3 minutes after the heating current had been switched off. Similar results were obtained to those mentioned above. The thermionic measurements for Curve 4, Fig. 6, were then made, after which the photo-electric readings shown in Table VII, in Curve 12, Fig. 4 and in Fig. 7. Before each photo-electric measurement the strip was glowed to about $1,700^{\circ}\text{C}$. for 5 minutes.

TABLE VI.

ϕ almost unmeasurable. Slit 5/100 in. wide. Anode volts=7.5.

λ in \AA .U.		1,850	2,040	2,140	2,240	2,360	2,540
Electrometer readings at a time after switching off heating current of—	3 mins.	0	0	0	0	0	0
	4 mins.	0.8	1.8	2.3	0.2	0	0.5
	5 mins.	1.8	3.3	3.5	2.9	0.7	0.9
	6 mins.	2.7	5.0	7.2	6.2	1.9	1.5
	7 mins.	4.1	6.6	10.8	10.1	3.2	1.6
	8 mins.	5.4	8.4	14.3	14.9	5.9	2.2
	9 mins.	6.7	10.6	18.9	20.2	8.6	2.2
	10 mins.	7.5	12.5	23.0	27.5	12.6	2.4

From the curves in Fig. 7, the rate of growth of the photo-electric currents which growth takes place even in the best vacuum that could be obtained, can be deduced. After three minutes, the rate of growth is a maximum for λ =about $2,200 \text{ \AA}$.U. It is possible that if photo-electric measurements could be made imme-

Immediately after the platinum had cooled, no photo-electric currents would have been found to exist. Assuming, however, that the rate of growth of photo-electric currents for, say, 5 minutes after the heating current had been switched off, is linear, it would appear from the above results that photo-electric currents are produced by light of wavelength 2,040 Å.U. and 2,140 Å.U., but not for $\lambda=2,240$ Å.U. and above

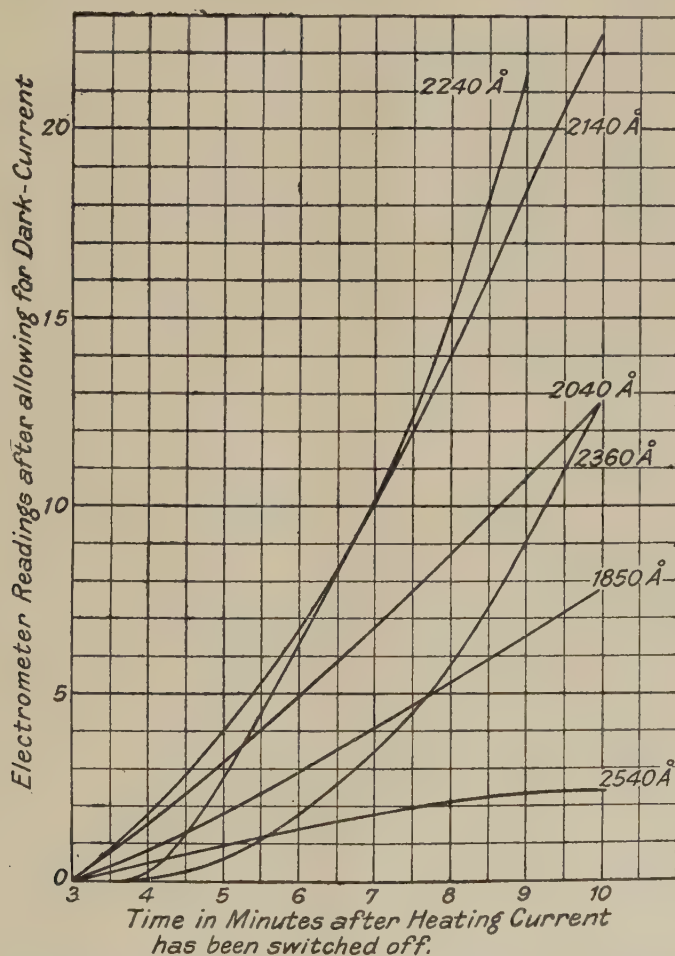


FIG. 7.—CURVES SHOWING RATE OF GROWTH OF PHOTO-ELECTRIC CURRENTS WITH TIME FOR GIVEN WAVELENGTHS AFTER THE SECOND PLATINUM STRIP HAS BEEN HEATED TO 1,700°C.

this. The sensitivity curve for $3\frac{1}{2}$ minutes after switching off the heating current is shown in Curve 12, Fig. 4, a noteworthy result being that there is no "foot" to the curve, but within the sensitivity of the apparatus there is a definite point where the photo-electric currents cease to be produced.

Another point is that in this curve there is no apparent maximum sensitivity within the range of wavelengths investigated.

GENERAL CONCLUSIONS FOR PLATINUM.

The photo-electric curves for platinum may be classified into four types.

- (1) Those found after a yellow hot glowing.
- (2) Those found within an hour or so of a white hot glowing.
- (3) Those found several hours after a white hot glowing.
- (4) Those found 3 minutes after a long glowing to a temperature approaching the melting point under the best vacuum conditions.

The thermionic curves can be classified into two groups.

- (1) Those corresponding to the "large-emission" state.
- (2) Those corresponding to the "small-emission" state.

Any intermediate states seem to be unstable, for the change over from the one state to the other only occupied a few minutes from the large to the "small emission" state, whilst from the small to the "large emission" state, the change was instantaneous if the pressure were suddenly but slightly increased by lowering the liquid air from the trap for a fraction of a second. If the platinum were hot and in the "small emission" state and the heating current were switched off, on gradually reheating the strip it was found that the new thermionic currents for relatively low heating currents were larger than they would have been if the platinum had remained in the "small emission" state, but that on heating the platinum to a higher temperature, a very rapid reversion to the "small emission" state would occur. It thus seems very likely that the "large emission" state thermionic results correspond to the second class of photo-electric sensitivity curves, while the thermionic "small emission" state corresponds to the fourth class of photo-electric curves. It was impossible to find thermionic curves to correspond to the photo-electric states 1 and 3, since the glowing always changes these to states 2 and 4.

Identifying the photo-electric states 2 and 4 with the "large" and "small emission" states the results may be classified as shown in Table VII.

TABLE VII.—*Photo-Electric and Thermionic Work Functions of Platinum.*

First Strip.								Second Strip.							
Large emission state.				Small emission state.				Large emission state.				Small emission state.			
Thermionic.		Photo-electric.		Thermionic.		Photo-electric.		Thermionic.		Photo-electric.		Thermionic.		Photo-electric.	
ϕ	λ_0	ϕ	λ_0	ϕ	λ_0	ϕ	λ_0	ϕ	λ_0	ϕ	λ_0	ϕ	λ_0	ϕ	λ_0
3.77	3,275	4.65	2,650	4.09	3,010	3.61	3,420	4.65	2,650	4.88	2,530	5.48	2,250
*4.33	2,850	3.52	3,500	4.07	3,030	4.27	2,890
3.97	3,110	4.23	2,900	3.42	3,600	5.17	2,390
...	3.97	3,110
...	4.08	3,020
...	3.62	3,410
...	3.76	3,280

* This value is believed to be too high on account of the thinning of the strip, which was not accounted for.

On the whole it seems that the thermionic work function for platinum in the "small emission" state is if anything slightly higher than for the "large emission" state, whilst the photo-electric work function is much higher for the former state.

In all cases the photo-electric work function is higher than the thermionic, but the difference is much more marked for the "small emission" state. For the "small emission" state, the photo-electric work function is measured three minutes after thermionic measurements have been made under the best vacuum conditions, and the photo-electric work function is undoubtedly for this state over 30 per cent. greater than the thermionic.

Whatever may be the cause of the variations in the work functions, there can be no doubt about the fact that heat treatment increases the photo-electric work function more than the thermionic. It reduces the thermionic currents to about one-thousandth of their previous value, and also the photo-electric sensitivity considerably, but while the thermionic work function is but slightly increased, if at all, the photo-electric work function is considerably increased. Another effect of the heat treatment is to decrease greatly the photo-electric sensitivities in the "foot" of the curves, so that eventually this "foot" ceases to exist (within the sensitivity of the apparatus), and the curve is more nearly in accordance with the theoretical curve of Professor Richardson based on the principles of statistical equilibrium*.

The results in the photo-electric curves are very similar to those obtained by Sende and Simon,† Suhrmann,‡ and Tucker,§ but differ from those of Welo.|| Apparently, however, Welo did not heat his platinum foil to a sufficiently high temperature for a sufficiently long time to obtain the condition which is termed above the "small emission" state. One difference between the above results and those of Sende and Simon, Suhrmann and Tucker is that in the above results the effect of a white hot glowing is not only to increase the sensitivity, but also to decrease temporarily the "long-wave" limit.

It should be noted that Sende and Simon, and Tucker both find that immediately after platinum is cooled after an intense heating, the light from a mercury vapour lamp produces only about one-thousandth of the previous photo-electric current, and that they come to the conclusion thereby that the true long-wave limit of platinum is very little, if any, greater than $1,850 \text{ \AA.U.}$

Whilst the above results do not show such a marked decrease in the long wave limit, yet they do suggest that under some conditions it might be reduced to less than $2,250 \text{ \AA.}$ Tungsten also shows the same property of producing relatively large photo-electric currents under some conditions which disappear after a strong heating.

It might be suggested that the strong heating of platinum merely reduces the photo-electric currents without altering the long wave limit. This is not so, for it is seen that the strong heating reduces the sensitivities at longer wavelengths to zero, whilst at shorter wavelengths the reduction is only slight.

* Richardson, *Phil. Mag.*, 23, p. 615, and 26, p. 549.

† Sende and Simon, *Ann. der Physik*, 65, p. 697 (1921).

‡ Suhrmann, *Ann. der Physik*, 67, p. 43 (1922).

§ Tucker, *Phys. Rev.*, December (1923).

|| Welo, *Phil. Mag.*, 45, p. 593 (1923).

GENERAL CONCLUSIONS.

In conclusion, it must be said that the above results show that the photo-electric work function of platinum is greater than the thermionic, very definitely so when the platinum for both measurements is in the state referred to above as the "small emission" state. For tungsten, no definite results were obtainable in respect of this question; and if the tungsten is in the same state for both thermionic and photo-electric measurements, the results here show no reason for supposing the two work functions to be different. Nevertheless tungsten and platinum are alike in their behaviour in so far as strong heating of either of them increases its photo-electric work function. The greater part of the "foot" of the photo-electric sensitivity curves appears to be due to the state of the surface of the metal, perhaps to gas, since under the better vacuum conditions it dwindled away and finally vanished.

In conclusion, I should like to take this opportunity of thanking Professor Richardson for suggesting these experiments and for his helpful advice during their course.

DISCUSSION.

Prof. O. W. RICHARDSON said that the Paper sets more problems than it solves. The rate of growth of photo-electric activity with time and various other points need further investigation. The author's original aim was to settle the identity of the thermionic and photo-electric work functions, but he had been baffled by the effects of obscure changes in the surfaces of the specimens. Previous work had been done by Young and the speaker with potassium, but this metal was unsatisfactory to work with, and it had been expected that more definite results would be obtained with less easily contaminated metal surfaces. The surprising results actually obtained opened up considerable possibilities of further research.

Prof. A. O. RANKINE pointed out that the two work functions were more likely to be identifiable if they were measured under the same experimental conditions as to temperature. Would it not be preferable to be content with a much smaller thermionic current and to measure it with the electrometer, so as to equalise the temperature conditions? The view that threshold potentials are very definite quantities did not seem to be borne out in the present instance.

Dr. J. H. VINCENT said that in the photo-electric experiments the asymptotic "foot" of the curve showing the dependence of photo-electric current on wavelength was presumably restricted by the difficulty of getting sufficiently intense low-frequency radiation directed upon the filament inside the enveloping anode. Would it not be possible to insert an additional filament into the tube and to use this as a source of radiation? The results would be rough on account of the mixed character of this radiation, but the conditions would be substantially black-body conditions and some idea of the wavelengths involved could thus be obtained. Had not the substance of the present results been obtained by Prof. Richardson in his original investigations made twenty-five years ago?

Dr. LEWIS SIMONS said the author seemed to have succeeded in controlling the changes in photo-electric sensibility very easily; but, personally, he had found great difficulty, when dealing with very slow electrons, in controlling the nature of the metal surfaces satisfactorily. The extreme variability of the emissivity of metal surfaces perhaps had a bearing on the work of De Broglie and Whiddington on the verification of the quantum theory for irradiation by X-rays, where the nature of the surfaces has not been particularly studied. Would the author say how far it had been possible to keep the pressure constant in experiments lasting a considerable time in view of the fact that the results had been found so extremely sensitive to slight changes of pressure? In conclusion, he would suggest that since the photo-electric current is carried by electrons moving with mixed velocities, its interpretation is very doubtful: the energy of this current would be a far more significant quantity.

Dr. E. H. RAYNER said he would like to make an addition to Prof. Rankine's suggestion. Would it not be possible to reduce a given photo-electric current to, say, half its value, and then restore the original strength by a change of temperature? In this way thermionic and photo-electric measurements could be made under conditions as nearly as possible identical.

Mr. W. V. MAYNEORD (communicated): It is desired to bring to the notice of the author of the Paper by Woodruff (*Phys. Rev.*, Vol. 26, p. 655, November, 1925) on the Photo-electric Emission from Platinum,

Effects similar to those obtained by Mr. Harrison are described, fresh specimens dipped in nitric acid being photo-electrically inactive, but restored by heating to 250°C. by an electric current through them, though heating in an oven to a higher temperature did not restore sensitivity. An interesting point arising from the results due to Woodruff is that the specimen rendered insensitive by heating to a very high temperature (say 1,300° K) was yet sensitive to the radiation from a tungsten filament within the tube, showing that the insensitiveness appears to be due to a shift of the threshold to wavelengths less than those transmitted by quartz. Again, a specimen heated to 1,300° K for 17 hours showed no emission under the action of a mercury lamp for two months though air was often admitted and pumped out again. Restoration is effected by moderate heating, as above. Many other phenomena and relevant details are discussed by Woodruff, whose results are in many respects similar to those described in this Paper.

AUTHOR'S reply (communicated): I am glad to have had brought to my notice the Paper by Woodruff, whose results when compared with mine are very interesting. The same variability in both work functions is found in both cases, and so far as the effect of heat treatment concerned there appears to be perfect accord between Woodruff's results and mine. Woodruff's samples of platinum, however, are more electro-negative than mine both thermionically and photo-electrically; his photo-electric currents are much smaller than those I obtained, for whilst in many cases he obtained no photo-electric current even with the full light of a quartz mercury vapour lamp or iron arc, there was always a fairly large photo-current in similar circumstances in my experiments. Similarly, in Woodruff's results, the thermionic work function ϕ is given in three cases as 5.34, 6.12 and 9.22 volts respectively, whereas in mine in no case was there a value of ϕ exceeding 5.17 volts, the average value being about 4.0 volts. Further, my thermionic measurements were made over a more extended range of temperature.

It is difficult to see why two samples of platinum obtained from different sources should not be equally electro-positive, for the only difference in treatment between the two cases is that Woodruff's samples were treated with nitric acid whereas mine were not. The behaviour of Woodruff's platinum is very similar to that of my first tungsten sample, both photo-electrically and thermionically.

With regard to Professor Rankine's, Dr. Vincent's and Dr. Rayner's suggestions, it now appears that Woodruff attempted to measure both the work functions for the same temperature, and that he employed an additional tungsten filament inside his photo-electric tube. It is obvious that, at any rate for tungsten, photo-electric measurements need to be made using radiation of wavelengths shorter than those transmitted by quartz, and possibly more use could be made of some internal source of ultra-violet radiation, such as a tungsten filament.

With regard to Dr. Simon's remarks, in order to obtain the energy of the photo-electric current a knowledge is required of the distribution of energy and mean energy of the electrons at each wavelength used. I have no experimental data in this respect. By the use of liquid air, the pressure can be kept constant for at least two days, and very often for three days, at a value below the detecting limit of a McLeod gauge.

XXVI.—THE ANALOGY BETWEEN RIPPLES AND ACOUSTICAL WAVE PHENOMENA.

By A. H. DAVIS, *D.Sc.*, Physics Department, The National Physical Laboratory.

ABSTRACT.

The extent of the analogy between cylindrical sound waves and waves on the surface of a liquid is studied. It is established for inviscid media that as regards velocity potential the differential equations are similar provided the disturbance is small and is harmonic in type. It is then shown that the velocity potential in a field of inviscid surface waves may be used to represent that in a field of cylindrical sound waves, provided the size of any obstacle bears the correct relation to the wavelength of the disturbance. In the case of a liquid having a depth greater than half the wavelength, it further follows that the height of a surface wave is a measure of the condensation of air in the corresponding acoustical condition.

The effect of moderate viscosity is of the same type for sound waves and for surface waves; it is most marked for short wavelengths, and it decreases amplitudes without appreciably altering the wavelength. The decrease in amplitude depends upon the viscosity, and upon the time which has elapsed since the commencement of free oscillations, or, for maintained oscillations, since the disturbance concerned left the source. For surface waves further damping occurs if the depth is less than half a wavelength, and the apparent viscosity may be appreciably increased by contamination of the surface by means of a film of oil of excessive thinness. Viscous effects are generally negligible in the case of sound, but they are appreciable for the water waves that would usually be used in a small ripple tank not greater than, say, 10 ft. in size. Mercury waves are much less affected by viscous damping than water waves.

Experiments conducted with model obstacles in a ripple tank showed that the effects of the meniscus around the obstacle and of the amplitude of the source were not important. When the water becomes stale on exposure—and presumably contaminated—the relative distribution of ripples around obstacles is appreciably modified, but not to an extent which would correspond to any very marked change in the loudness of a sound.

Experiments have also been conducted, outside the limits of strict mathematical analogy, using an impulsive disturbance instead of a maintained train of waves. When it is recognised that a sound pulse travels out singly, whereas with ripples subsidiary wavelets accompany the main pulse, the correspondence between ripple photographs and sound pulse photographs is most striking.

Illustrations are given of the use of a ripple tank in connexion with architectural acoustics, and of its general value where wave phenomena are concerned.

GENERAL wave phenomena are somewhat elusive to the imagination and water waves have frequently been used to illustrate them. Tyndall⁽¹⁾ made early use of ripples for this purpose in connexion with the propagation of light. Later Vincent⁽²⁾ obtained his well-known photographs giving examples of reflection, refraction, diffraction and interference: he studied the analogue of an optical zone plate and of a simple diffraction grating, and his ripple measurements agreed well with the usual formulæ.

Ripples in a small tank appear, also, to be specially suitable for illustrating acoustical phenomena, for in these the wavelength is usually comparable with the size of any objects concerned. As early as 1844 we find Scott Russell,⁽³⁾ in connexion with the acoustics of buildings, referring to the study of the behaviour of sound by using the water wave analogy, and pointing out that, in general, ripples are not completely analogous to sound waves. Watson⁽³⁾ and Michel⁽⁴⁾ have studied the acoustic features of buildings by such means, and a ripple tank has been in use for this purpose at the National Physical Laboratory for some time. The object of this Paper is to elucidate the conditions under which the analogy is valid and to illustrate its use.

Taking the axis of z vertically downwards, the equation of continuity and the condition of zero vertical motion at the level bottom $z=l$ are both satisfied by⁽¹⁰⁾

$$\varphi = \varphi_1 \cosh k(z-l) \quad \dots \dots \dots (8)$$

where

$$\frac{\partial^2 \varphi_1}{\partial x^2} + \frac{\partial^2 \varphi_1}{\partial y^2} + k^2 \varphi_1 = 0 \quad \dots \dots \dots (9)$$

Obviously φ_1 represents a disturbance to which the disturbance at any depth z is proportional, the constant of proportionality falling off rapidly as the depth increases. It may be noted that this control condition is of the form desired for analogy to cylindrical sound waves. It remains to find the value of k .

In terms of φ the pressure condition for small motions⁽¹¹⁾ is

$$\delta p / \rho = gz - \partial \varphi / \partial t \quad \dots \dots \dots (10)$$

where ρ is the density of the fluid, and g the acceleration due to gravity.

If h denote the elevation of the surface at the point x, y , and T the constant surface tension, the pressure at the surface due to capillarity is $-T(\partial^2 h / \partial x^2 + \partial^2 h / \partial y^2)$. Consequently, from (10) the pressure condition at the free surface is

$$\frac{T}{\rho} \left(\frac{\partial^2 h}{\partial x^2} + \frac{\partial^2 h}{\partial y^2} \right) = gh + \frac{\partial \varphi}{\partial t} \quad \dots \dots \dots (11)$$

except perhaps within a meniscus at a boundary, where the surface tension force cannot be regarded as vertical. Differentiating with respect to t and noting the kinematical surface condition,

$$\partial h / \partial t = -\partial \varphi / \partial z \quad \dots \dots \dots (12)$$

the surface pressure equation takes the form⁽¹¹⁾

$$\frac{T}{\rho} \left(\frac{\partial^3 \varphi}{\partial x^2 \partial z} + \frac{\partial^3 \varphi}{\partial y^2 \partial z} \right) = g \frac{\partial \varphi}{\partial z} - \frac{\partial^2 \varphi}{\partial t^2} \quad \dots \dots \dots (13)$$

Applying equation (8) to this, a relation for the surface is obtained which, for harmonic motion $\partial^2 \varphi / \partial t^2 = -\omega^2 \varphi$ satisfies (9) provided k has the value given by

$$\omega^2 / k^3 = (Tk / \rho + g / k) \tanh kl \quad \dots \dots \dots (14)$$

Thus for small harmonic surface waves, the general equation for the disturbance at the surface of the liquid is

$$\frac{\partial^2 \varphi}{\partial x^2} + \frac{\partial^2 \varphi}{\partial y^2} + k^2 \varphi = 0 \quad \dots \dots \dots (15)$$

It is readily shown⁽¹¹⁾ from (12) that the velocity c of propagation of harmonic surface waves is given by $c = \omega / k$. Obviously $k = 2\pi / \lambda$, as was also the case with sound waves.

At rigid boundaries we have the condition

$$\partial \varphi / \partial n = 0 \quad \dots \dots \dots (16)$$

The Analogy.

We have thus seen that the differential equation

$$\frac{\partial^2 \varphi}{\partial x^2} + \frac{\partial^2 \varphi}{\partial y^2} + k^2 \varphi = 0 \quad \dots \dots \dots (17)$$

is satisfied for harmonic disturbances both by cylindrical sound waves and by waves upon a water surface.

The general theory of functions of this type shows that the potential ϕ_P at any point P within a region to which the equation applies is determined by the values of ϕ and of $\partial\phi/\partial n$ at the boundary. The formula is⁽¹²⁾

$$\phi_P = -\frac{1}{4} \int D_0(kr) \frac{\partial\phi}{\partial n} ds + \frac{1}{4} \int \phi \frac{\partial}{\partial n} D_0(kr) ds \quad \dots \quad (18)$$

where the integrations are performed around the boundary and where $D_0(z) = (2/\pi) \int_0^\infty e^{-iz \cosh u} du$.

Now in considering equation (18), we may note that for a family of boundaries of similar shape but of different size the directions of the normals ∂n at corresponding points will be the same; further, at rigid boundaries $\partial\phi/\partial n$ has the value zero both for sound waves and for ripples. The values of kr at corresponding points within the different boundaries will be the same provided r varies as $1/k$ —that is, provided r varies as λ ; or, in other words, if the linear dimensions of the model boundaries are proportional to the wavelength of the disturbance set up within them.

Consequently, if we have two similar regions in which this scale relation is satisfied, and to which equation (17) applies—say a region of sound waves and a region of ripples—and if we arrange the disturbance at the boundaries of the two regions to be such that values of ϕ and $\partial\phi/\partial n$ correspond, then the disturbance ϕ_P at all corresponding points within the region will correspond exactly.

Having established this analogy in terms of velocity potential, we may show that within a certain limitation the height h of ripples may be taken as a measure of the condensation s of air at the corresponding point in a sound field. The complete analogy is between hk and s .

We have from 2

$$s = \frac{1}{c^2} \frac{\partial\phi}{\partial t} \quad \dots \quad (19)$$

As regards ripples, however, we see from (11) that in general h is not simply proportional to $\partial\phi/\partial t$, owing to a term involving the curvature of the disturbed surface. However, from (12) and (8) we find $\partial h/\partial t = k\phi_1 \sinh kl$. Consequently, for harmonic disturbance we have $\partial^2 h/\partial t^2 = k \sinh kl (\partial\phi_1/\partial t) = -\omega^2 h$. Applying this result to a combination of (8) and (11), and using (14), we find that the curvature $(\partial^2 h/\partial x^2 + \partial^2 h/\partial y^2)$ is equal to $-k^2 h$.

It then follows that (11) may be written in the form

$$hk = \frac{1}{c^2} \frac{\partial\phi}{\partial t} \quad \dots \quad (20)$$

provided $\tanh kl = 1$, as is approximately the case when the depth of liquid exceeds half the wavelength.

On comparing (19) and (20) we see that for ripples of a given wavelength (since $k = 2\pi/\lambda$) the height of a ripple is a measure of the condensation of air at a corresponding point in the acoustic field.

Effect of Viscosity and Allied Phenomena.

The introduction of viscosity complicates the equations both for sound waves and surface waves.

Stokes⁽¹³⁾ first evaluated the effect of viscosity in the case of sound. For plane harmonic sound waves it is found that the amplitude of free waves dies away exponentially with time t , being proportional at any instant to $(^{14}) e^{-t/\tau} \cos(\omega t + \epsilon)$, where $\tau = 3/2\nu k^2$, and ν is the kinematical viscosity of the air. For the case where a constant disturbance $u = a \cos \omega t$ is maintained in the plane $x=0$, we find $(^{15}) u = ae^{-x/l} \cos \omega(t - x/c)$ where $l = c\tau$. The wave amplitude diminishes exponentially as it proceeds. It will be noted that, since $l = c\tau$, the decay in amplitude suffered in reaching a distance x from the source is that calculable from the time modulus τ and the time interval t involved. In both proofs $1/kc\tau$ is assumed small. For sound waves in air this condition is satisfied, and, if λ be expressed in centimetres, we find $l = 9.56 \times \lambda^2 \times 10^3$. The effect of viscosity on amplitude is thus very slight except for sounds of very short wavelength.

Kirchhoff⁽¹⁶⁾ showed that a further cause of dissipation of sound energy is to be found in the thermal processes consequent upon alternate rarefactions and condensations of air. A complete investigation taking into account this thermal effect as well as viscosity shows that the effect is equivalent to an increase in the kinematic viscosity ν , but the order of the effect is unchanged.

The effect of viscosity on harmonic surface waves is similar to that for sound. By a method which applies when the depth is greater than, say, half the wavelength, Lamb⁽¹⁷⁾ shows that the wave velocity is unaltered by viscosity, and that the time modulus of decay τ in this case is given by $\tau = 1/2\nu k^2$, provided $1/kc\tau$ is small. The condition is usually satisfied for mobile liquids unless the wavelength is excessively small. Presumably, in fields of continuously maintained harmonic ripples, the total viscous attenuation attained in reaching a given point would be given by the factor $e^{-t/\tau}$, where t is the time which has elapsed since the ripple in question left the source. If this is so, relative intensity values along a wave front would not be affected in spite of the general attenuation experienced by the wave.

Expressing τ in terms of λ , and evaluating in the case of water, we find approximately $\tau = \lambda^2$ seconds.*

Table I gives details of waves on clean water of depth greater than half the wavelength.

TABLE I.—Surface Waves on Water.
(Depth greater than $\lambda/2$.)

Frequency. per sec.	Wavelength. cm.	Velocity. cm. per sec.	Number of oscillations in which amplitude falls to $1/e$ of its undamped value.
3.5	13	45.3	590
5.0	6.55	33.2	220
7.5	3.46	26.1	91
10.0	2.38	23.8	57
13.2	1.73	23.2	41
20	1.20	23.9	29
30	0.87	26.0	23
50	0.59	29.8	18
100	0.36	36.7	13

* The modulus τ is the time in which the ripples decay to $1/e$ of the amplitude they would have in the absence of viscosity.

The effect of viscosity is seen to be appreciable for water waves of short wavelength. The use of long waves would involve an unduly large ripple tank.

For mercury we find $\tau = 10\lambda^2$, a value about ten times as great as the value for water, so that viscous effects are much reduced when mercury* is used. For general use mercury has, however, the disadvantage that the surface is not easy to clean, and the cost of large areas of sufficient depth is considerable. A clean water surface can be obtained very easily by simply refilling the cleaned tank with a fresh supply.

The effect of contamination of a wave surface depends upon the nature of the contamination. The general effect would be to alter the surface tension, and thus to affect the relation between wavelength and velocity. This in itself would not affect the validity of the analogy, provided the relation between the wavelength and the scale of the model were preserved. However, there is a special form of contamination, such as that in which an exceedingly thin oil film, say, not more than one or two millionths of a millimetre in thickness, covers the water thickness. The calming effect of such a film appears to be due to the increase of surface tension of the film which occurs when its thickness is reduced by stretching. Assuming that such a film of oil renders the wave surface practically inextensible, Lamb calculates the time modulus of decay⁽¹⁸⁾ $\tau = (8/\omega\nu k^2)^{1/2}$. The ratio of this to the modulus obtained on the hypothesis of constant surface tension is assumed small; for water it is approximately equal to $(2/\lambda c)^{1/2}$. The calming effect of such excessively thin films would be very great; thicker films would not show the effect.

II. EXPERIMENTAL.

Various experimental arrangements have been used from time to time in the production and study of ripples. The late Lord Rayleigh⁽¹⁹⁾ developed the first accurate method of studying ripple phenomena; to render visible the very small disturbances of the surface he used a modified form of Foucault's method of testing plane surfaces. Further, he used the stroboscopic method for making the waves appear to stand still.

Reference has been made already to the work of Tyndall and of Vincent, who used ripples to illustrate wave motion. A style attached to a vibrating tuning fork was used to generate the waves. Shultze⁽²⁰⁾ devised a novel electrical method of producing ripples which Pfund⁽²¹⁾ and Palmer⁽²²⁾ have developed further. Waetzmänn⁽²³⁾ generated waves by intermittent puffs of air, and Watson and Shewhart,⁽²⁴⁾ using a modification, obtained some interesting photographs of wave phenomena.

In the present apparatus the waves were generated by means of a style attached to an electrically maintained tuning fork. The ripples were viewed by intermittent flashes of light isoperiodic with the oscillations of the style. The following details of the apparatus may be of interest.

The ripple tank was about 3 ft. by 5 ft. in size, and 2 in. deep, the bottom being of plate glass. For the experiments water was introduced into the tank, usually to a depth of about 2 cms. For the wavelengths used this depth was sufficient to satisfy the requirement $l > \lambda/2$ referred to in establishing the analogy to acoustical propagation and in evaluating the viscosity effect. The style used to agitate the

* Values of wavelength and velocity corresponding to a given frequency are nearly the same for mercury as for water. If the suffix m relate to the wavelength at which the velocity is a minimum, we have in centimetre units the following values for water and for mercury: Water: $\lambda_m = 1.73$; $c_m = 23.2$; $n_m = 13.4$. Mercury: $\lambda_m = 1.27$; $c_m = 19.9$; $n_m = 15.7$. Relations between c/c_m , λ/λ_m and n/n_m are the same for all mobile liquids.

water was a copper wire 0.2 cm. in diameter, with a gently rounded end. Provided the wire was fairly vertical on entering the water, and the tip was just about level with the water surface, excellent ripples were attained, spreading equally in all directions from the source. Excessive amplitudes of vibration of the fork resulted in streaming of the water and distortion of the ripple circles.

As regards the frequency of the fork, we have seen that the longer the wavelength the less important the viscous damping. However, long waves necessitate large tanks, and in the tank available the lowest frequency used was consequently about 20 vibrations per second. This corresponds to a wavelength of 1.2 cm. Incidentally in this region the group velocity $U = c - \lambda(dc/\partial\lambda)$ differs but little from the wave velocity. To obtain an adequate number of ripples in the tank a higher frequency of 50 per second was usually necessary; this gave approximately half the wavelength associated with the slower fork.

To render the wave visible intermittent light from an electric arc about 10 ft. distant was passed vertically upwards through the glass bottom of the tank, and cast a shadow of the waves upon a horizontal screen suitably mounted about 5 ft. above. The intermittence was secured by means of a stroboscopic sector disc driven in synchronism with the tuning fork by means of a 10 volt phonic motor. The slots in the discs occupied about one-eighth of the total area, so that during any flash the wave advanced not more than one-eighth of a wavelength. The ripple pattern upon the screen was photographed. By using a translucent screen the pattern could be photographed from above with no fore-shortening. Actually, however, it was photographed from below from the side of tank; distortion was largely corrected by setting the illuminating beam at a slight angle to the vertical, or by using the falling back of the camera.

The height of the screen was chosen to give good definition for waves at a distance from the source, since chief interest was centred in them. No one position is equally satisfactory for all amplitudes. In ripple photographs given later (Figs. 2 and 3) the blurring near the source arises from this choice of screen distance, not from any imperfections of the waves.

There is not necessarily any simple relation between the amplitudes of two unequal ripples, and the optical density of the two corresponding regions in the photograph. In interpreting the subsequent photographs one must in general be content to assume that when two portions of the same photograph are equally intense, they relate to regions of equal wave amplitude.

As will be seen later continuous waves were not always employed. Fig. 1 gives a general view of the ripple tank, and shows a round-headed dipper which was used to generate short pulses. In operation it was merely withdrawn from the water by electromagnetic means; vibrations and consequent splashing were prevented by the brass leaves between which the dipper slides. A model section of a building of which the reflecting characteristics of the outline were required, is shown in the water lying flat upon the glass bottom of the tank. The inclined beach shown to the left of the tank prevents reflections of waves from this end. This property of a beach was pointed out by Dr. Vincent.

Diffraction Measurements.

Experiments were carried out to determine the characteristics of continuous water ripples. In preliminary work some diffraction patterns were studied. Six

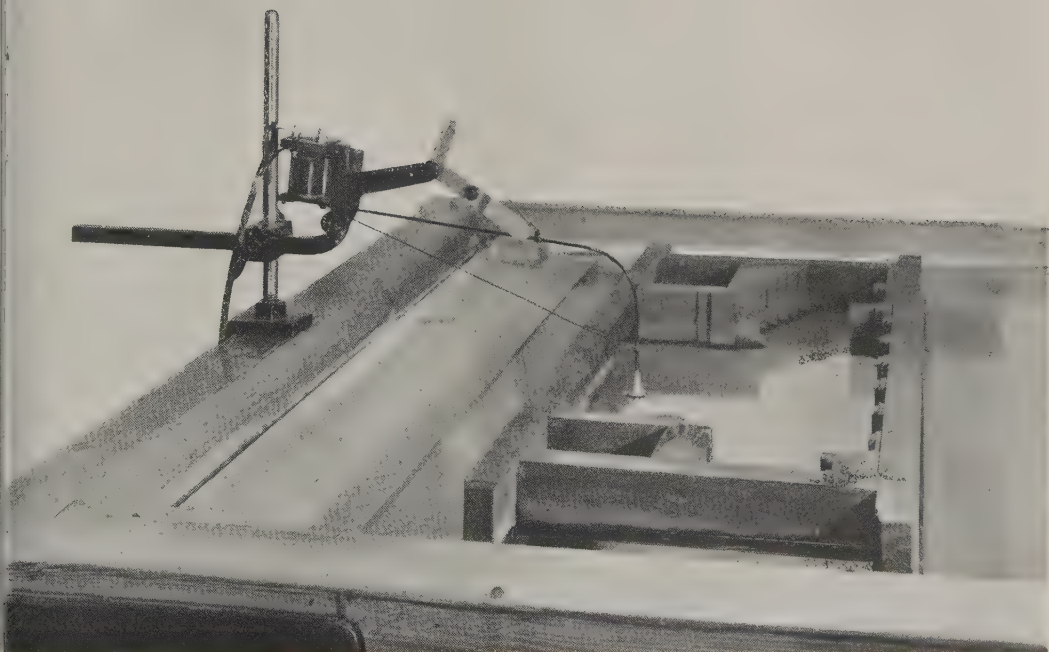


FIG. 1.—RIPPLE TANK.

To face page 240]

points spaced 2 cms. apart, and fixed to a straight bar were carried on a tuning fork, so that all six points agitated the water. An interference pattern was set up, and measurements were made of the directions of the maximum and minima of intensity, with the following result :—

—	1st max.	1st min.	2nd min.	3rd min.	4th min.	5th min.
Theoretical	37°	30°	24°	18°	12°	6°
Observed	36°	32°	25°	16°	10°	Not visible.

The spectra resulting from two diffraction gratings of ten slits were then observed. One grating had slit-widths of 1 cm., the other of 2 cms. In each case the opaque portions of the grating were 1 cm. wide. First order and second order spectra were studied in the two cases, with the following result :—

—				Observed spectra.		Wavelength.	
						Calculated.	Observed.
1st Grating	1st order	22°	0.75	0.86
				2nd order	63°	0.89	
2nd Grating	1st order	15.5°	0.80	0.86
				2nd order	28°	0.70	
				3rd order	53.5°	0.80	

The above measurements* were made on a screen before photographic arrangements were developed. The angles were necessarily measured rather closer to the grating (50λ to 100λ) than is usual in optical experiments. In view of the errors possible under such circumstances the agreement is quite good. The experiments have not been repeated.

Screening by an Obstacle.

In order to study the effect of varying conditions in the ripple tank, photographs were taken under various circumstances of the bending of ripples around a standard obstacle. The obstacle was placed in the tank at a definite distance from the centre of disturbance. Photographs were taken of the distribution of ripples revealed. Observation was made of the intensity of the waves on the photograph at some standard screened position, and measurement was made on the photograph of the distance from the source at which unobstructed ripples attained this same intensity. For each condition tested—fresh or stale water, large or small fork amplitude, etc.—the intensity at a screened position was thus expressed in terms of a distance from an unscreened source. For this work the normal obstacle was 6 cms. by 5.9 cms. in size, and the wavelength of the ripples was about 0.6 cm.

Effect of Meniscus around Obstacle.

Experiments were conducted to ascertain whether the water meniscus around the model affected the bending of waves around it. Increasing the size of the obstacle should presumably lessen the importance of any meniscus effect, but when the scale of an experiment was doubled, no appreciable difference was observed. An attempt was also made to vary the meniscus effect by greasing the model.

* I am indebted to Mr. N. Fleming, B.A., for these measurements.

Two types of experiment were conducted. In the first ripple distributions were photographed before and after the model was greased. Generally speaking, there was no appreciable difference, and the maximum deviation observed was an increased intensity at the standard screened position corresponding to a 10 per cent. decrease in distance from an unobstructed source. This type of experiment has the disadvantage that the surface of the liquid is not in the same state for the two photographs. Special photographs were consequently taken in which a source was placed symmetrically with respect to two similar models, one of which had been greased. Fig. 2 shows two such photographs taken with identical disposition of apparatus. In one the left-hand model is greased, and in the other it is the right-hand one. No appreciable difference is visible.

Effect of Amplitude of Fork.

Under various conditions photographs were taken for different values of fork amplitude, avoiding as far as possible amplitudes so excessive as to cause streaming of the water and distortion of the ripple circles. In some cases it is thought that slight distortion did occur. On the average, varying the fork amplitude did not affect relative intensities in different parts of the field: in some cases slightly increased bending was recorded, in others a slight decrease. Variations in relative intensity at the screened position did not exceed that covered by a ± 10 per cent. change in distance from an unscreened source.

Effect of Condition of Water Surface.

Fresh clean water gives a larger field of ripples than water which has become dusty, etc., through exposure in the tank for several hours. The reduced amplitudes in the latter case are presumably due to a viscosity effect, consequently they should be associated with an apparent increase of intensity in screened regions as compared with unscreened. For if the intensity appears to be the same at two points, one screened and one unscreened, the screened region is at a smaller path distance from the source, and has undoubtedly suffered less from viscous diminution.

An hourly series of photographs was taken during one day to reveal the extent to which the bending of ripples around an obstacle was affected by the surface contamination referred to. Fig. 3 shows four photographs covering an interval of twenty-four hours. On each photograph of an identical set of prints two standard screened positions, A and B, were marked, and measurements were made of the distances at which unobstructed ripples appeared to reach the intensities at these standard positions. Table II summarises results as estimated:—

TABLE II.—*Effect of Exposure of Water Surface.*

Time in Hours.	Distance at which unobstructed ripples reach the intensity of the standard screened positions (wavelengths).	
	A	B
0	—	47
4	42	28
7	32	23
24	30	25

The standard positions A and B were at path distances from the source of 21.3λ and 16.3λ respectively. The wavelength did not alter with time. In the

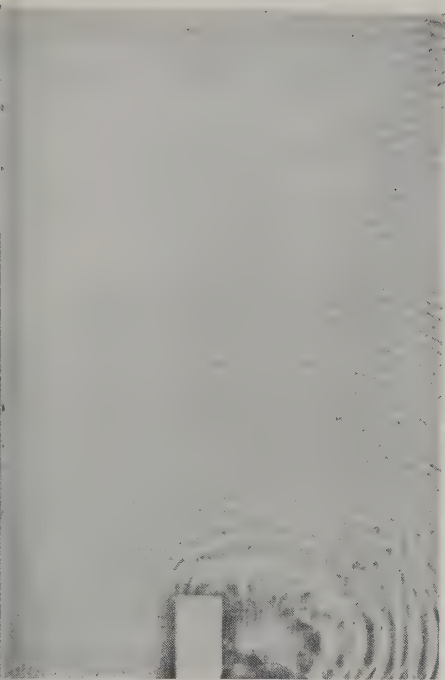


Right-hand Model greased.



Left hand Model greased.

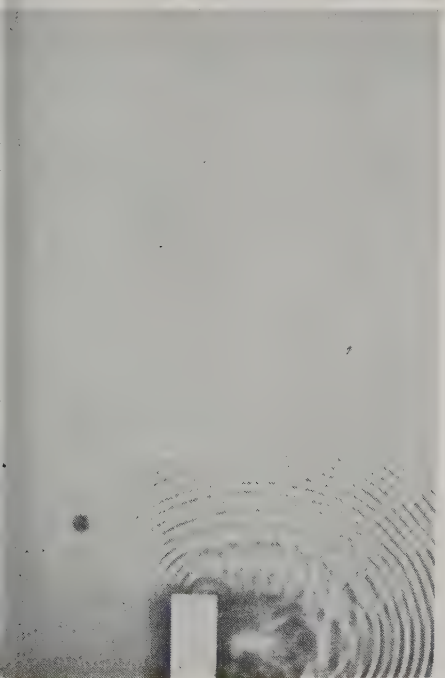
FIG. 2.—EFFECT OF GREASING MODEL.



0 Hours.



4 Hours.



7 Hours.



24 Hours.

FIG. 3.—EFFECT OF EXPOSURE OF SURFACE OF WATER.



Ripples.



Sound Pulse.

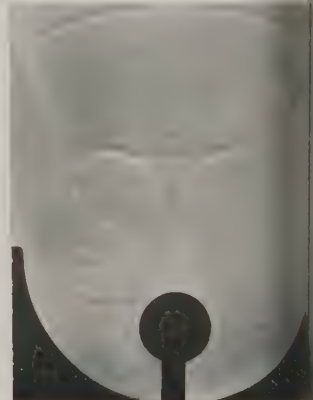
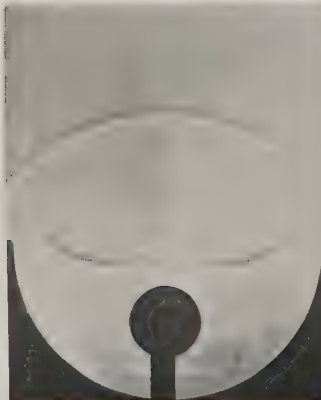
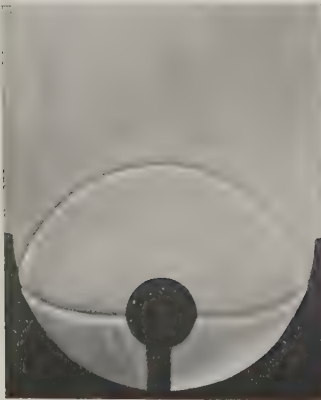
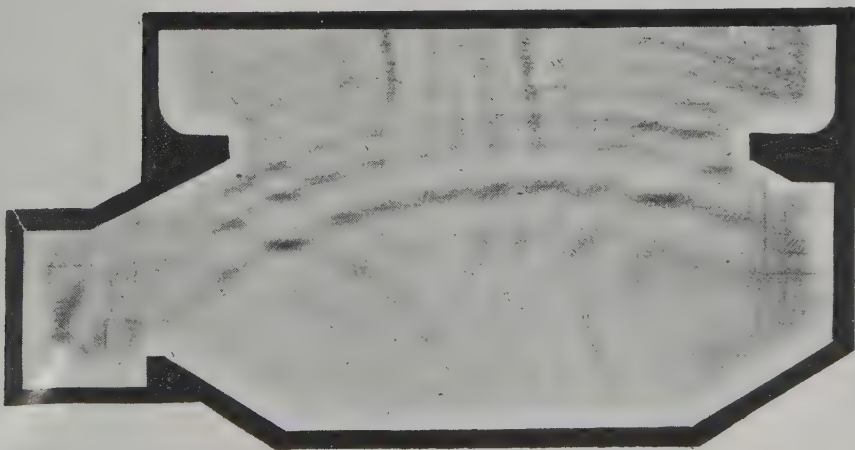
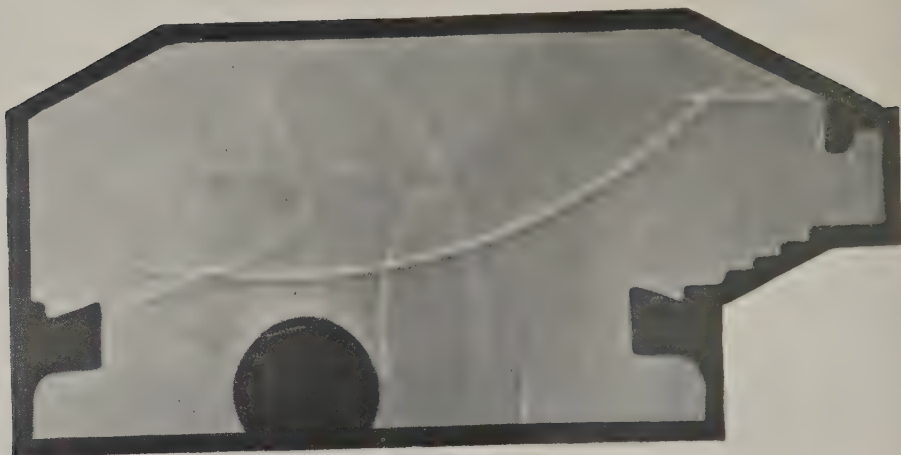


FIG. 4.—COMPARISON BETWEEN RIPPLE AND SOUND PULSE PHOTOGRAPHS RELATING TO REFLECTION FROM A HEMICYLINDRICAL MIRROR.

FIG. 5.—SOUND PULSE AND RIPPLE PHOTOGRAPHS RELATING TO ACOUSTICS OF BUILDINGS.
(c) Gallery under Separate Ceiling

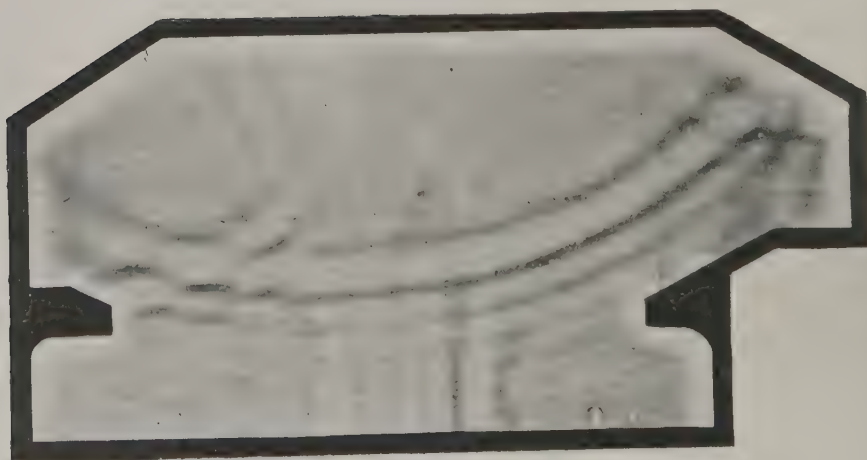


SOUND PULSE PHOTOGRAPH.



(a) Gallery under Main Ceiling.

RIPPLE PHOTOGRAPHS.



(b) Gallery under Main Ceiling.

same case of very stale water, the apparent bending of ripples is appreciably less, for unobstructed ripples reach the intensity of the standard screened ripples in about one half the distance required with fresh water.

From theoretical considerations, we have seen that even for fresh water appreciable viscous decay of ripples will occur. The present experiments show that when a surface is exposed to the air of the room its apparent viscosity increases after a few hours. Consequently relative intensity measurements are somewhat unreliable at points having markedly different distances from the source. No indications have been given, however, that the intensity relations from point to point along a wave front are altered by viscous effects.

Wave Pulses.

So far discussion has been confined to the case of harmonic waves continuously maintained, for which the analogy between surface waves and sound waves is seen to be so close. In studying the directions in which a wave front is reflected or diffracted—a problem which arises for instance in dealing with acoustics of buildings—it is much more convenient to trace the history of a single pulse or short train of waves than to attempt to interpret the complicated pattern which would arise from the use of continuous waves. In some respects surface waves and sound waves differ in behaviour when pulses are concerned. A sound pulse travels out singly, but in the case of an impulsive disturbance of a water surface a number of smaller ripples travel in front of the main pulse. In spite of these differences—which would greatly complicate the equations of the analogy—both are essentially wave motions of a more or less impulsive type, and some close correspondence in behaviour is to be expected.

Fig. 4 compares results obtained by means of the ripple tank with some actual sound-pulse photographs obtained by the Toepler-Boys-Foley method. Both relate to a disturbance due to a source at the focus of a hemicylindrical mirror. The photographs have been taken at approximately equivalent time intervals after the origin of the wave. They show the outgoing circular part of the wave front and also the part which has been reflected from the mirror. In each case the reflected wave is seen to be a plane wave modified at its extremities by spherical aberration.

In Fig. 5, photographs (a) and (b) compare ripple and sound-pulse photographs showing the behaviour of waves after reflection from boundaries representing the longitudinal section of a hypothetical council chamber. The ceiling is at the top of the photograph, and extends over the galleries at each end. The position of the speaker—indicated by the large black circle in the sound-pulse photograph—is practically the same in both cases, and the distances travelled by the waves correspond almost exactly. The sound-pulse photograph is clearer because it deals with only a single pulse instead of a short train of waves, but when this is recognised the correspondence between the two photographs is most striking, not only as regards ceiling reflection, but as regards the extent and direction of reflections from subsidiary surfaces.

Relative Uses of a Ripple Tank.

The use of a ripple tank is mainly to demonstrate the propagation of waves in various cases. It may be used to demonstrate to students and others the behaviour of waves at plates or diffraction gratings, etc., or to architects the reflecting characteristics of the boundaries of a proposed building.

In Fig. 5, photographs (b) and (c) illustrate an application to the study of the acoustics of buildings. They show the desirability of putting the gallery under the main ceiling of the council chamber concerned. If ceilings are low enough, they do not give rise to distinguishable echoes; indeed, reflections of sound from the ceiling contribute usefully in raising the level of loudness in regions reached. Ceiling reflection is particularly desirable in large council chambers where speeches may be delivered from any part of the floor, for no other reflecting surface would be equally effective for all speakers. In the photograph 5(b) we see the ceiling reflection spreading to benefit people even in the rear of the right-hand gallery; in 5(c), where the roof has been modified so that the gallery is under a separate ceiling, this useful reflection to the back is cut off.

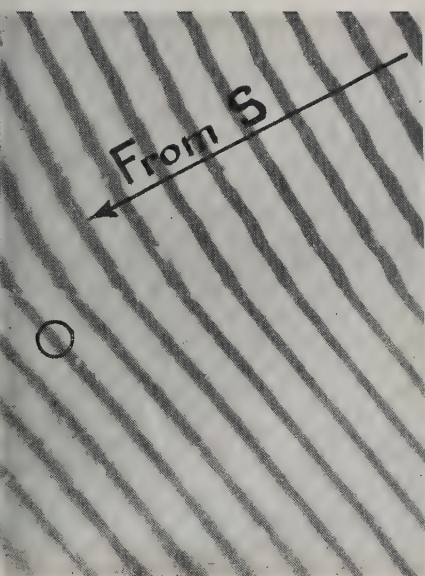
Figs. 2 and 3 illustrate a case of screening on a scale which might arise with a source of sound near a building or buildings in the open air. In this case the analogy must not be pushed too far, for we have seen that the viscosity of the water affects the apparent screening. However, very considerable changes of sound intensity are necessary to modify in any marked manner the sensation of loudness, and cases may well arise in which the moderate differences arising from viscosity are not important.

The final photograph, Fig. 6, illustrates certain simple wave phenomena at a boundary that may lead to error in the apparent bearing of the source. It is of interest in connection with errors in direction-finding by wireless waves as observed at a station near the sea coast.^(2,5) Conditions corresponding to any change of velocity of waves on crossing the boundary were attained by providing one-half of the tank with a false bottom only slightly submerged. In the photographs the boundary is clearly apparent. The direction of the source S has been indicated by an arrow, and a point O has been marked to represent the position of an observing station. In Fig. 6(a), which relates to the case of a source and observing station on opposite sides of a boundary, the apparent direction change is evident. In Fig. 6(b), where source and observing station are both on the low-velocity side of the boundary, the condition at the observing station is seen to be complicated by the presence of an internally reflected wave. In both cases the apparent bearing of the source is further towards the top of the page than its true position.

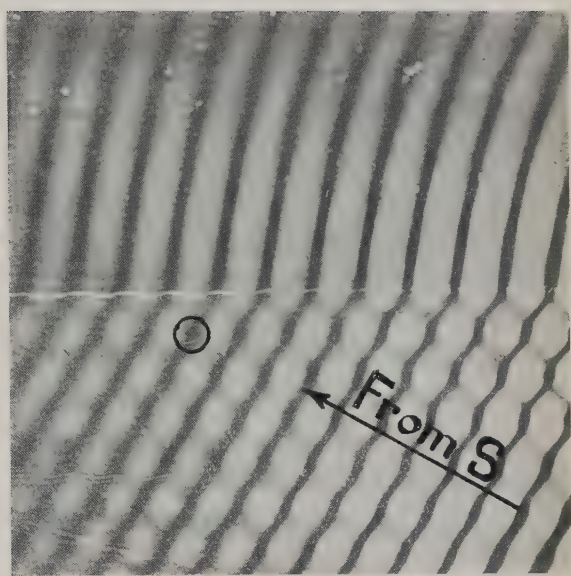
The author desires to thank Mr. N. Fleming, B.A., for his assistance referred to in the text and in connexion with the sound-pulse equipment and technique. Mr. R. Berry, Junior Observer, assisted with the experiments and photographs.

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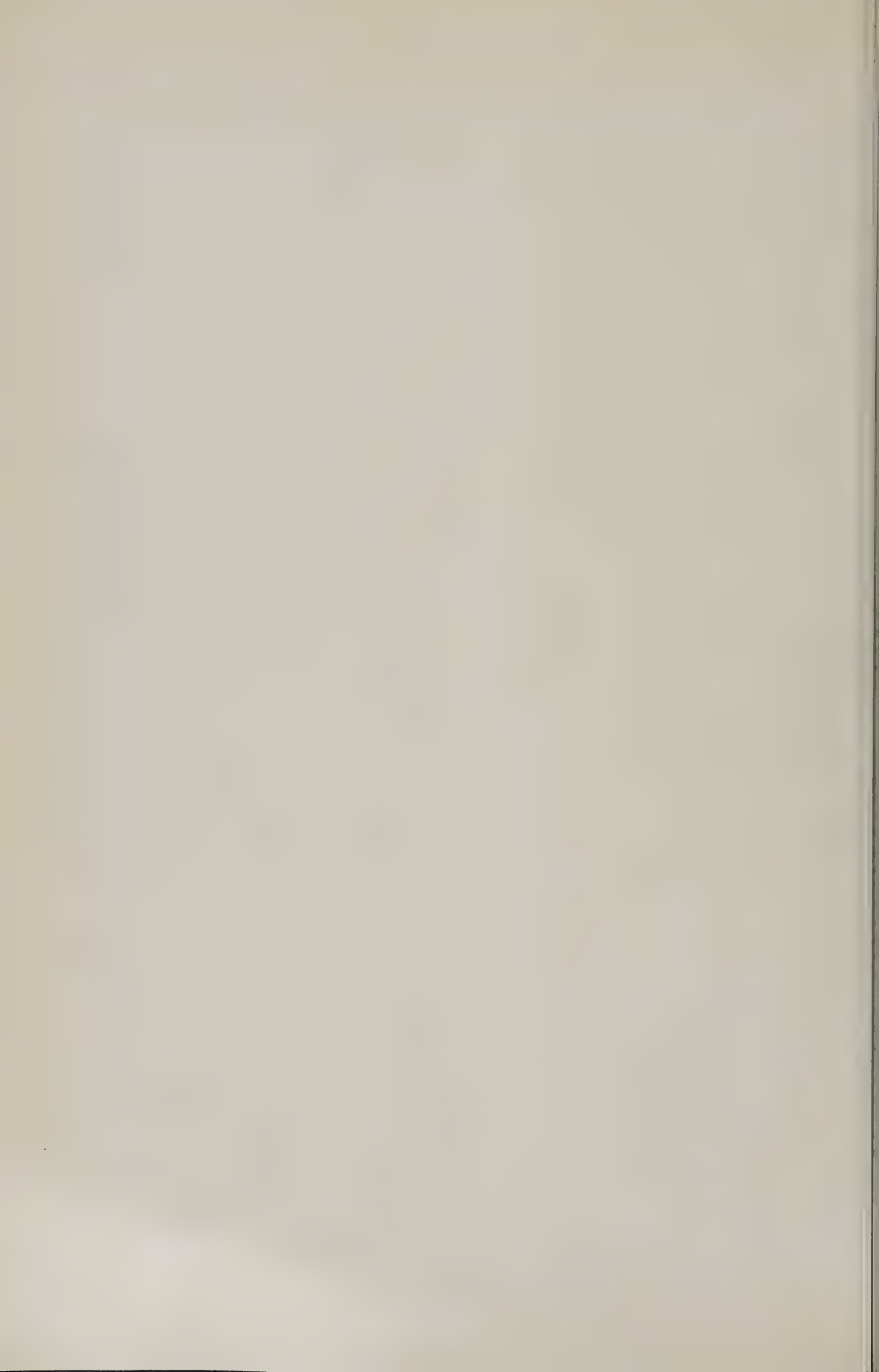


(a)



(b)

FIG. 6.—WAVE PHENOMENA NEAR A REFRACTING BOUNDARY



- (10) Lamb. Loc. cit., Art. 257.
- (11) cf. Rayleigh. Loc. cit., Art. 353.
- (12) Lamb. Loc. cit., Arts. 302-305.
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- (17) Lamb. Loc. cit., Art. 348.
- (18) Lamb. Loc. cit., Art. 351.
- (19) Rayleigh. Collected Papers, 3, p. 383.
- (20) Shultze. Zeits. f. Instk., p. 151, 1907.
- (21) Pfund. Phys. Rev., 32, p. 324, 1911.
- (22) Palmer. Phys. Rev., 33, p. 528, 1911.
- (23) Waetzmänn. Phys. Zeits, 12, p. 866, 1911.
- (24) Watson and Shewhart. Phys. Rev., 7, p. 226, 1916.
- (25) Smith-Rose. Nature, 116, p. 426. 1925.

DEMONSTRATION.

The author, assisted by Mr. Berry, illustrated the Paper with a demonstration in which (a) continuously emitted ripples were viewed stroboscopically under conditions illustrating refraction and also diffraction by a grating, round a screen, and through apertures of various sizes; and (b) single pulses, internally reflected within a wooden enclosure, representing the vertical section of an auditorium and laid in the ripple tank, were viewed by instantaneous illumination.

DISCUSSION.

Major W. S. TUCKER said that the Author had described an elegant method for solving practical acoustic questions which it would be difficult or impossible to handle mathematically. In the neighbourhood of aerodromes great inconvenience was caused by the noise made by the running up of engines before flight. The author had attacked this problem, at Major Tucker's request, by means of a model illustrating the screening due to a hangar, the wavelength employed being produced to scale, and the ratios of the intensities at various points in the shadow being estimated as described in the Paper. The speaker exhibited some of the photographs obtained in this connexion. It must be borne in mind, however, that the two-dimensional solutions given by the Paper do not necessarily give safe guidance in the case of three-dimensional problems. The speaker illustrated this point by a further slide, showing by polar diagrams the calculated distribution of intensity in the neighbourhood of a sound source screened by placing it (a) midway between two parallel plates and (b) inside a tube of diameter equal to the distance between the plates, so that the two systems are identical in section. In this extreme case two entirely different sound distributions are obtained.

Dr. J. H. VINCENT congratulated the Author on his learned and delightful Paper. He would have thought that, for all purposes except refraction experiments, a reflecting surface like that of mercury would have been preferable to the water surface actually used. The meniscus effect at the edges of a screen can in a mercury tank be eliminated by making the screen of thin cover glass and allowing it to float on the mercury. For refraction effects mercury is unsuitable, however, because on account of the cost of the metal the dimensions of the apparatus have to be small, and the reduction of depth necessary to exhibit refraction effects cannot be achieved because of the tendency of mercury to gather into drops of a certain minimum depth on a surface which it does not wet. Amalgamated submerged surfaces have therefore to be used as screens, and their position cannot conveniently be photographed.

Mr. E. G. RICHARDSON said that the impulse method seemed to him more satisfactory than the ripple method for studying the acoustics of buildings, and it had, he believed, been

more extensively used by Sabine for that purpose. In filming plays in which wrecks occur it used to be the practice to photograph a sinking model boat, but usually no attention was paid to the scale of the ripples, with the result that the waves seen were sometimes longer than the boat. The method of scaling adopted by the author would have been useful in such cases, but it appeared to be the practice, under the financial conditions which now obtain in America, to sink full-size vessels.

Mr. M. D. HART said that the author spoke in the second paragraph of his Paper of the value of "ripples in a *small* tank," but would not experiments on a larger scale be more satisfactory? He would like to ask how the measurement of the ratios of the intensities in different regions of a sound shadow were carried out.

AUTHOR'S reply: I naturally agree with Major Tucker that two dimensional solutions of acoustic problems have limitations; indeed, in stating that the strict analogy is between ripples and cylindrical sound waves, some limitations to general use are implied. Particularly caution must be observed where interference phenomena are prominently involved, as in the special cases quoted by Major Tucker. However, ripple tank results appear to be useful, for instance, in connection with the acoustics of buildings of not too complicated shape. Here it is desired to ensure that the shape of a section shall tend to reflect sound to certain regions rather than to others; the question of the interferences which may arise in regions reached by the sound is of subsidiary importance and probably where articulate speech is concerned of no importance at all. With respect to the size of the tank, a larger one would be advantageous for reasons indicated in the Paper, but would be somewhat unwieldy. The present tank is quite large enough to deal with model sections of buildings on a scale of $\frac{1}{2}$ in. to 1 ft., and on this scale the distance from crest to crest between successive ripples in the impulsive train corresponds to sounds having a frequency of 200-700 per second, a region in the speech range. Dr. Vincent's remarks on the use of mercury are very interesting. It should be noted that the use of mercury does not greatly alter the wavelength-velocity-frequency relations, but for a given degree of damping a wavelength may be used of about one-third of that required with water. Thus relatively large tanks may still be desirable, and one must decide in any case whether the convenience and cheapness of clean water do not justify its adoption. The models were photographed in position after removing the water, in order to avoid blurred outlines; the same method might be employed in a mercury bath having amalgamated submerged models, of the kind mentioned by Dr. Vincent. When ripples are studied instead of sound pulses, the complete progress of waves may be observed visually or followed in detail by the kinema camera; further, modifications of the model may be studied rapidly by adjusting the position of loose parts. For photographic presentation of results sound pulse photography is much clearer. Intensity distributions in a shadow may be studied by judging by eye at what distance from the source in the unscreened region of the photograph, the photographic intensity of the ripples is the same as that at any given screened point.

XXVII.—ON THE EVAPORATIVE LOSSES OF VACUUM-JACKETED VESSELS OF THE DEWAR TYPE.

By R. M. ARCHER, *A.R.C.Sc., B.Sc., M.I.E.E.**Received February 4, 1926.*

ABSTRACT.

In this Paper the evaporative losses of metal Dewar vessels are discussed, and particulars given of experiments made by the author in Oxygen Laboratory of the Air Ministry. The separation of neck and radiation losses is described, and also a method of testing adsorbents under working conditions. Experimental details are given with graphs and tables.

INTRODUCTION.

VERY little information regarding the vacuum-jacketed Dewar flask was obtainable until 1918, apart from that given in a few Papers by Professor Dewar himself, and some structural details derived from examination of vessels of foreign make. Towards the end of that year certain monographs prepared by the late Dr. Harker and his associates were available in the Oxygen Laboratory of the Air Ministry, and were published subsequently in an abridged form by the Oxygen Committee of the Department of Scientific and Industrial Research. These Papers dealt mainly with the theory of vacuum flasks and other heat-insulated vessels, but the need of improving existing types and of working out methods of evacuating them in bulk is mentioned also. The importance of testing the performance and characteristics of glass and metal vacuum flasks and of drawing up specifications is pointed out, and it is stated that "at present complete data concerning any one vessel are lacking." The action of the adsorbent is only considered very briefly in the monographs, and no reference is made to the difficulty of removing gases from it and from the walls of the vessel, nor to the rise of pressure and evaporative rate which occurs after long use.

In October, 1918, the author had occasion to report upon the adsorptive power of activated charcoal and devised simple apparatus for making a preliminary examination. A large burette containing the dry gas under test (usually air) was connected at the bottom to a movable mercury reservoir, and at the top to a small bulb of the adsorbent, which could be immersed in water or in liquid oxygen. Allowance having been made for the contraction of the gas in the unfilled part of the bulb (by making a dummy experiment with the bulb partially filled with a non-adsorbent) the volume of gas taken up at atmospheric pressure, and in some cases, at reduced pressure, was found; and in the report the need for making measurements at very low pressures was emphasised. Samples of wood and fruit stone-charcoal were examined, and their apparent density found; and somewhat later tests were made with precipitated copper, copper oxide, pumice, fine sand, pith, lycopodium, and other substances.

The method of testing the adsorbent under working conditions which is described in this Paper is based upon the general experience of the Air Ministry Oxygen Laboratory in 1918 and the first half of 1919; but the author in 1920, when working

out details of bulk evacuation and leak testing, found it desirable to include long period tests (taken after sealing), and in some cases to put the adsorbent into an external metal capsule, and to connect vessels in parallel while under examination.

Also, the use of a sensitive reflecting flowmeter was found subsequently to be necessary in special cases.

In the calculation of neck losses given in the Harker monographs no account was taken of the cooling action of the vaporised oxygen.

Banneitz, Rhein and Kurze, in a comprehensive Paper on vacuum flasks, refer to this action, but state that in certain experiments they made the results were inconclusive. Briggs, in a Paper on the Dewar vessel,[†] describes experiments made on temperature gradients in the inner necks, and mentions some early tests on containers with short necks. Temperature gradients are mentioned also by Griffiths, Hagen and Rubens,[§] in Papers published in 1900 and later, drew attention to the influence of wavelength and of temperature on the reflecting power of various surfaces, and showed that in certain cases, an increase in wavelength may cause the reflecting power of two surfaces to become more nearly equal. (Thus a change of wavelength from 450 $\mu\mu$ to 700 $\mu\mu$ increased the amount of radiation reflected from silver in the ratio $\frac{94.6}{90.6}$, the corresponding ratio for copper being $\frac{90.7}{48.8}$.)

Harker and Groom, in the Papers previously mentioned, state that reflecting powers of surfaces vary in a very irregular way with the wavelength. "Values of emissivity, deduced from determination of the reflecting power made under normal conditions have little validity, when applied directly to the conditions obtaining in the vacuum flask."

They point out that direct determinations for long waves are very difficult and that relative measurements by experiments on flasks "suffer from the disability that it is difficult to disentangle the effects of pure radiation from those of conduction." In consequence of uncertainty as to the correct values under working conditions they use, in their examples, "best" and "probable" values, and values deduced by theory from a knowledge of electric conductivity. As in the design of vacuum flasks a knowledge of the normal gas conduction, radiation and neck losses is required, and estimation of the effect of dust, oxide, solder, and defective polishing on the radiation losses is of great practical importance, determinations under working conditions are essential.

In the present Paper experimental data relating to a number of standard vacuum-jacketed metal vessels have been given, and the aim of the methods described has been to find a solution of the problem of "disentangling" experimentally all the chief sources of loss.

The author would like to take this opportunity of thanking the Air Ministry and the Department of Scientific and Industrial Research for leave to publish the information given in this Paper.

* "Investigations with Regard to the Principles of Construction of Containers for the Transport of Liquid Gases," (translation) *Annalen der Physik*, 4th Series, Vol. 61 (1920).

† "An Experimental Analysis of the Losses by Evaporation of Liquid Air contained in Vacuum Flasks," *Proc. Roy. Soc. Edinburgh*, Vol. 41, Pt. 2, No. 10 (1921).

‡ *Trans. Faraday Society*, 18, Dec. 1922, p. 230.

§ Report of the Oxygen Research Committee, Department of Scientific and Industrial Research, 1923, paragraph 37, Table IV.

I. SOURCES OF LOSS.

Since the rate of evaporation of the cold liquid in a Dewar vessel depends upon the rate at which heat reaches it, an experimental determination of the efficiency of the flask should include a measurement of the individual losses due to the entry of heat by each of the principal routes. The chief losses are due to :—

- (a) Conduction along the material of the inner neck.
- (b) Conduction through the residual gases in the space between the envelopes or shells.
- (c) Convection in these residual gases.
- (d) Conduction and convection in the vapour above the liquid.
- (e) Radiation between the opposing surfaces of the shells.
- (f) Radiation through the aperture of the inner neck.

In metallic vessels of normal proportions the inner neck, which is usually of nickel-silver or cupro-nickel, is long and narrow, and the error due to neglecting (f) is small. Convection in the residual gases is negligible also even in a vessel which has been evacuated only moderately. As regards the vapour itself the chief effect to consider is its abstraction of heat from the inner neck. This action makes it difficult to find either experimentally or by calculation, the net amount of heat which reaches the liquid by conduction down the neck.

In this Paper it is assumed that the vessels are of normal type, and that under normal conditions heat can reach the liquid in the following ways only :—

- A. By conduction across the residual gases.
- B. By radiation between the envelopes.
- C. By conduction through the substances of the inner neck (cooling action of vapour taken into account). The losses dealt with under this heading are called "neck losses."

A and B are practically independent of one another and of C. But C is a function of A and B.

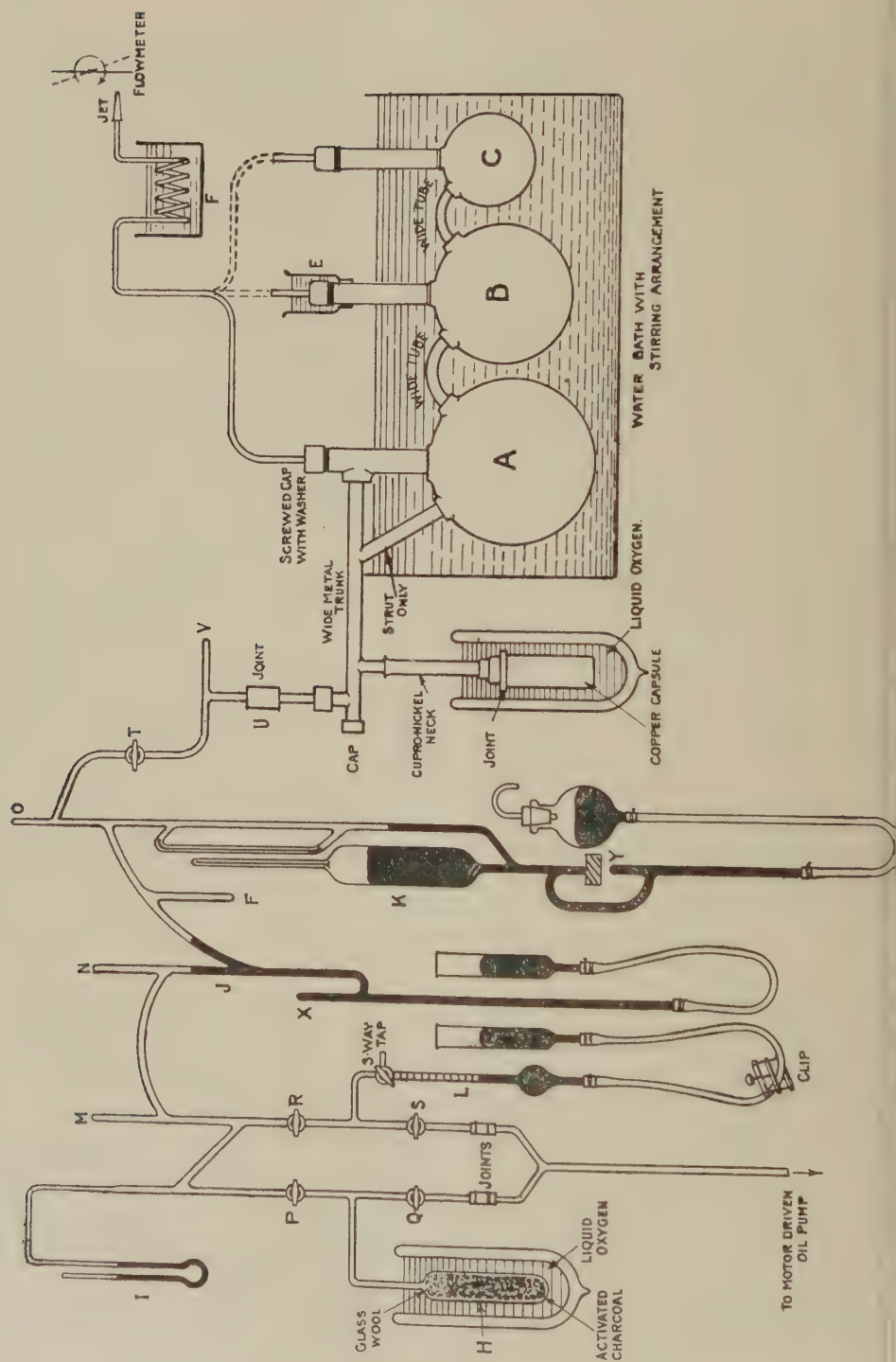
The method of evaluating the losses, which will now be described, has been applied to vessels of 25, 5, 3 and 1 litre capacity, and has yielded also some useful information regarding the vacuum-improving power of certain adsorbents.

II. APPARATUS AND PROCEDURE.

(A) Apparatus.

The vacuum flask *A*, Fig. 1, is placed in a water bath and the space between the envelopes connected to an evacuating system by a metal pipe, a special vacuum joint *U* being made between the metal and the glass parts of the system. Connected to the system is a large McLeod gauge *K*, an Anschütz gauge *I*, with a special air trap,* a tube *H* of activated charcoal, a gas-injection apparatus *L*, and a mercury seal *J* controlled by a movable reservoir of mercury. High vacuum taps *P*, *Q*, *R*, *S* and *T* are provided, and there are air traps at *X* and *Y*. Accessory glass apparatus such as drying tubes may be blown on to the blind tubes *F*, *M*, *N*, *O*, *V* if required. The system may be evacuated by a motor-driven "oil" or "mercury" pump connected below *S*, or by the charcoal bulb in the well-known way. If *P* is closed

* "A Simple Regenerative Vacuum Device and some of its Applications," H. P. Waran, Proc. Phys. Soc., London, Vol. 35, Part 4, June 15 (1923).



and Q opened the charcoal may be out-gassed without interfering with the rest of the evacuating system.

In some experiments the adsorbent to be used in the Dewar flask itself is placed in its usual position in the internal cup, but this is not always done when it is necessary to vary its amount or to replace it by another one. Removal and replacement of the outer copper envelope of a normal flask would involve repolishing the reflecting surfaces, and might alter the constants of the vessel. Also much time would be lost and the conditions might change appreciably. In such experiments the adsorbent is placed in an external metal capsule (Figs. 1 and 2), which may be opened and closed quickly and easily by using an annular soldered joint. The capsule, which is fitted with a dust filter, has a long nickel silver neck, and may be heated strongly, or may be cooled by liquid oxygen. It is easy to insert or remove the adsorbent without disconnecting the flask from the system or moving the bath. Further, the flask and its capsule may be sealed permanently, removed as one unit and tested independently.

When a comparison has to be made between different flasks they are sometimes connected together by short wide pipes and tested simultaneously, as at A , B and C , Fig. 1. This is better than testing them independently. Equality of pressure is secured, and the residual gases have the same composition, and therefore the same thermal conductivity in all the vessels.

In prolonged experiments, a trap immersed in liquid oxygen may be placed between the flask and the plant to prevent the deposition of mercury on the cold metal surfaces, with alteration of emissivity. (Hughes and Poindexter have shown recently that sodium or potassium may be used for intercepting mercury vapour.)*

In determining neck and radiation losses an electrical heater and other special apparatus is used.

(B) *General Method of Experimenting.*

(1) The space between the two envelopes is evacuated well, and the rate of evaporation of the cold liquid measured.

(2) Air or other gas is then admitted to the evacuated space in successive small charges of known amount. The initial and final effect of these injections on the pressure and rate of evaporation is measured.

(3) The changes of pressure produced by these injections when the vessel contains no cold liquid, or when it is heated, is measured also.

(4) In some cases the amount and nature of the adsorbent is varied.

(5) A sample of the adsorbent is placed in a separate glass vessel and its pressure-reducing power when cooled by liquid oxygen found. This experiment is conducted (a) at constant (atmospheric) pressure, (b) in a closed chamber in which the initial pressure is low, and the final pressure is of the same order as that in a Dewar vessel.

(6) Experiments are made for the determination of the neck and radiation losses.

(7) The flask is sealed and is filled and tested at short intervals over a long period—say once a fortnight for a year or more. The gradual rise in the rate of evaporation serves as a final check on the efficiency of the adsorbent and on the

* "Potassium as a Mercury Vapour Trap," *Phil. Mag.*, Vol. 50, August, 1925, No. 276.
(From Washington University, St. Louis, U.S.A.)

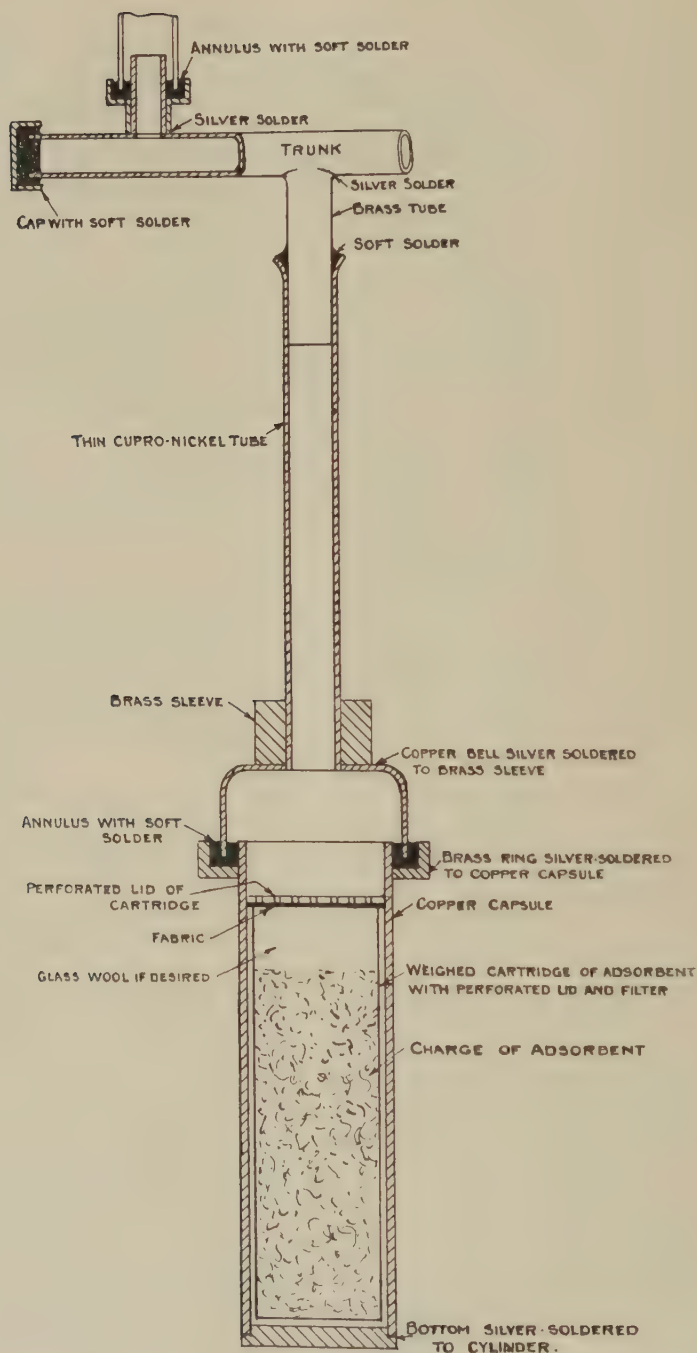


FIG. 2.—DETAIL OF CAPSULE D. EVAPORATIVE LOSSES IN VACUUM-JACKETED VESSELS OF THE DEWAR TYPE.

soundness of the vessel itself. If no formal adsorbent is used, a better measure of the rate of accumulation of gases is obtained; but the metal walls themselves appear to act as adsorbents to some extent.

(C) *Procedure in Specific Cases.*

(1) *Evacuation.*—The vessel was heated both internally and externally during evacuation, and drying was accelerated by phosphorus pentoxide. Evacuation was carried out by an oil pump or mercury pump, and was usually completed by a charcoal bulb in liquid oxygen. It was continued until the pressure was very low, and rose at a very small rate when the flask was isolated. (Full details are given in the Report of the Oxygen Committee, Department of Scientific and Industrial Research, 1923, §§171 to 202.)

In a few special cases the evacuated space was washed out by admitting oxygen gas and re-evacuating a few times, a process suggested by Dewar for removing residual gases not easily adsorbed by charcoal.

After evacuation the container was allowed to cool and the bath was placed in position. Liquid oxygen was then poured into the container and measurements of the rate of evaporation made. Simultaneous readings of the McLeod gauge were taken also. Observations were continued until the rates of change of the quantities became negligibly small.

In certain experiments on a container in 1920 the charcoal was very moist, and to avoid having to open the vessel vacuum distillation was used for removing the water. The rate at which water collected in a glass receiver gave some indication of the rate at which drying was proceeding. Use was made of a manometer also.

(2) *Observations.*—When the rate of evaporation had become constant, a small volume of dry air was drawn into the burette, and its volume at atmospheric pressure measured. It was then allowed to enter the evacuated system, and readings were taken as before, until the rate of evaporation had again become constant. As the volume of the evacuated space was known the amount of air which had entered the container could be calculated. Injections were continued to any desired extent, and in some cases the system was opened finally to the atmosphere.

The vacuum-improving power of the adsorbent was found by comparing the pressures of the residual gases when all parts of the vessel were at one temperature (say 15°C.) with the pressure when the inner shell held liquid oxygen. This was done in one of two ways:—

(a) After evacuation had been carried to any desired extent (say until the pressure, after cutting off the pump, remained steady at 10 mm., the temperature being 15°C.) liquid oxygen was introduced, and the steady values of the pressure and the rate of evaporation were noted.

Or

(b) When the rate of evaporation of the liquid became steady after a known amount of gas had been injected, the pressure was measured and the liquid oxygen was removed.

All parts of the vessel were then brought up to any desired temperature—usually that of the atmosphere, or that reached during evacuation—and the steady value of the pressure measured.

An advantage of method (b) is that the amount of gas held by the adsorbent is

known. It might have been calculated in case (a), but some assumption regarding the activity of the adsorbent would have had to be made.

Method (a) has the advantage that the order of the operations is the same as that followed during the evacuation of a container.

It is not always safe to assume that the order is immaterial, because hot copper gives up gases when heated, and occlusion appears to be slow and incomplete on cooling.

Equilibrium is not usually attained quickly. Charcoal evolves gases for many

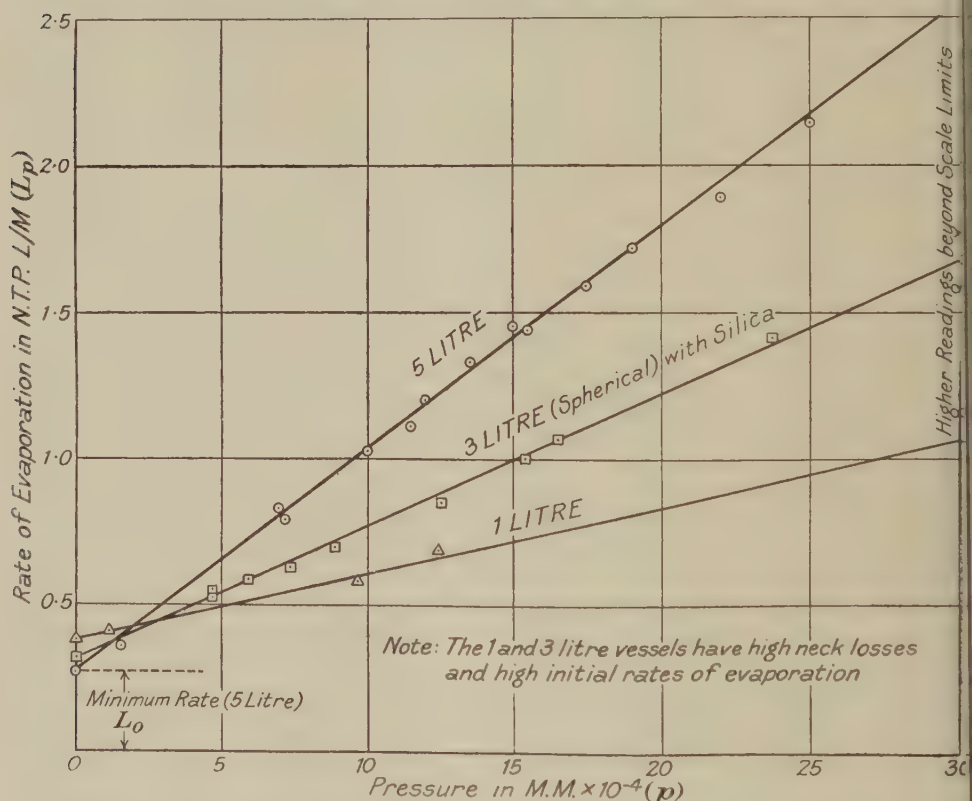


FIG. 3.—1, 3 and 5 LITRE COPPER CONTAINERS WITH CHARCOAL ADSORBENT OR SILICA. VARIATION OF EVAPORATIVE RATE WITH PRESSURE p .

days when in an evacuated vessel, and observations over such periods are seldom practicable. All that can be done is to wait until the rates of change are small.

III. GENERAL RELATIONSHIPS AND OBSERVATIONS.

(A) Relation between the rate of evaporation of the cold liquid and the pressure of the residual gases.

The relationship found for a 5-litre copper container examined in 1919 is shown in Fig. 3. After evacuation the rate of evaporation was measured and is regarded here as the minimum attainable. The corresponding pressure was too small to be

shown on the scale of the diagram. Known amounts of dry air were then admitted and the corresponding pressures and rates measured. The graph is nearly a straight line, so that the following equation is approximately true.

$$L_p = L_0 + Kp. \quad (1)$$

where p = pressure of residual gases when the vessel is in use (adsorbent very cold)
 L_p = rate of evaporation at pressure p
 L_0 = minimum rate of evaporation
 K = a constant.

Since $K = \frac{L_p - L_0}{p}$ it is numerically equal to the change in the rate of evaporation per unit change in pressure. The values actually obtained in the experiment were :
 $L_0 = 0.275$ litres of gas per minute (N.T.P.)

$$K = 0.0766 \text{ litres per minute per change of pressure of } \frac{1}{10,000} \text{ mm. mercury.}$$

Hence $L_p = 0.275 + 0.0766 p$ where p is in mm. $\times 10^{-4}$. (2)

The linear form of the equation, in conjunction with the known laws of gas conductivity, gives an explanation of the facts observed. At the lower pressures reached in the experiment the M.F.P. is conformable with the distance between the envelopes, and over the range tested the conductivity of the residual gas is approximately proportional to p . When p is very low the amount of heat transferred by gaseous conduction is small, and practically the only thermal input is that due to radiation and to neck conduction. It is of interest to find whether the observed increase in the rate of evaporation when gas is admitted agrees with the calculated increase.

Let R = the loss due to radiation, in litres per minute.

N = the loss due to neck conduction in litres per minute, assumed constant for all values of L_p

G = the loss due to gas conduction at pressure p , in litres per minute

H = number of calories conducted through the gas per second

M = mass of liquid evaporated by H calories

p = pressure due to the gas admitted in mm. mercury

θ_1 = temperature of the inner (cold) envelope (= 91°C. absolute)

θ_2 = temperature of the outer (warm) envelope (= 292°C. absolute)

A = area of the inner envelope (= 1,725 sq. cm.).

Then $H = Cp (\theta_2 - \theta_1) A$ (3)

where C is a numerical factor which is independent of the pressure and has a mean value which depends upon the temperatures of the envelopes.*

Also $L_0 = R + N$ (4)

C may be taken as about equal to 2.7×10^{-5} , the unit of pressure being 0.01 mm. mercury.

* Report of the Oxygen Research Committee, Department of Scientific and Industrial Research, 1923, paragraphs 23/26.

In later experiments it was found that the neck losses fell rather rapidly at first as the gas flow increased, but that the rate of fall soon diminished (Table IX.). The pressure/delivery graph should show, therefore, a slight upward concavity in its initial stages. In certain cases this is discernible, but the high percentage error of the McLeod gauge at low pressures makes it difficult to find the shape of the curve at points not far from the origin.

When the graph has once been found for any vessel the observed rate of evaporation gives a sensitive indication of the pressure. Advantage of this may be taken when several vessels are connected in parallel, or when one only is used for testing adsorbents.

(B) *Relationship between the rate of evaporation of the cold liquid and the equilibrium pressure reached during evacuation.*

In the experiments considered the adsorbent was activated fruitstone charcoal. Preliminary experiments in an evacuated glass vessel showed that, over a moderate range, there was a nearly constant ratio between the equilibrium pressure, P , when the charcoal was heated, and that, p , reached when it was cooled by liquid oxygen. P/p was found to depend upon the proportion which the mass of the charcoal bore to the volume of the space. Thus, if the vessel held 1 gramme of the charcoal per 10 c.c. of evacuated space P/p was 40,000 : 1. In the 5-litre vessel itself there was only about 1 gramme per 470 c.c. of space, but P/p was 20,000 : 1. Lower values of P/p were found in a few cases when p was increased, the ratio not being quite constant when the range of pressure variation was too wide. In one vessel examined there was about 1 gramme of charcoal per 221 c.c. of space, but P/p was only about 6,000 : 1, although p was low. It is probable that charcoal of inferior activity had been inserted in this case. See (F) (1).

As the main aim of the experiments was to determine the losses of the vessels, a full investigation on adsorbents was not undertaken. It is of interest to note, however, that the values of P/p (now known as the Pressure Reduction factor) obtained are of about the same order as those found subsequently in an investigation by Lambert.* The magnitude of P/p was found by him to depend upon a number of factors, and no simple law of its variation was discovered.

It must be remembered that when the adsorbent is in a metal envelope gases evolved or adsorbed by the metal itself introduce complications. Also the adsorbent power of charcoals and of activated silica varies considerably.

Taking $P/p=20,000$ for the 5-litre vessel considered and substituting for p in equation (2) we get :—

[illegible]

where P is expressed in mm. of mercury.

(C) *Characteristic equations for standard vessels with charcoal adsorbents.*

Equations (2) and (5) hold for the particular 5-litre vessel tested and may be regarded as two of its *characteristic equations*.

* Report of the Oxygen Research Committee, Department of Scientific and Industrial Research, 1923, paragraphs 81/86.

In the case of five other 5-litre vessels tested in 1919 the following mean values were obtained :—

$$L_0 = 0.24 \text{ L/M}$$

$$K = 0.079$$

$$P/p = 31,000 \text{ (when both expressed in the same units).}$$

Hence the characteristic equations of vessels of this type are :—

$$L_p = 0.24 + 0.079 \text{ } p \quad (6) \text{ (} p \text{ in mm.} \times 10^{-4} \text{)}$$

$$L_p = 0.24 + 0.0255 \text{ } P \quad (7) \text{ (} P \text{ in mm.)}$$

These vessels were all of the same type as the first, and the higher value of P/p is due to the fact that more charcoal was used.

Relationships of the same kind were obtained with 25 and 1 litre vessels. When the characteristic equations for a given type of vessel have been determined, it is evident that they may be used for calculating :—

(1) The equilibrium pressure which must be reached during evacuation to secure a given rate of evaporation ; or the rate of evaporation if the vessel has been sealed when the equilibrium pressure has reached a measured value.

(2) The pressure of the residual gases :—

(a) When the vessel contains the liquid.

(b) When it is empty and has reached atmospheric temperature : or

the rate of evaporation when the pressure has risen to some measured value after a long period—say a year.

Since in the experiments the amounts of gas injected were measured, the *effective* activity of the adsorbent under the special conditions which exist in a metal vessel has been found.

(D) Replacement of Charcoal by Activated Silica or Alumina.

The use of silica in vacuum vessels appears to have been first suggested by Professor Dewar, and data relating to the adsorptive power of silica gel and other substances at atmospheric pressure were published by Dr. Briggs in March, 1921.*

At that time no experimental data relating to the activity of silica at very low pressures, nor to its use in a metal flask, were available in the Air Ministry Laboratory. Somewhat later in 1921 the author made some tests with silica gel, alumina, and aluminium hydroxide, and prepared four metal flasks for long-period tests under working conditions. One contained no adsorbent, one alumina, and the others different charges of silica gel. (For details of periodic tests see D.S.I.R. Report, §§ 240 to 250.) It was found that at atmospheric pressure, and also at very low pressures, silica was a better adsorbent than alumina, but was inferior to charcoal.

Thus in one case silica gel was heated to about 130° C. for a long period, and when 1 c.c. was used per 163 c.c. of evacuated space, the values of P and of p were 0.17 mm. (mercury) and 0.83×10^{-4} mm. respectively. Hence $P/p = 2,000$ approximately.

A rough calculation based on the assumption that the pressure-reducing factor is inversely proportional to the volume of the space evacuated gives a result of about

* "The Adsorption of Gas by Charcoal, Silica, and other Substances," Proc. Roy. Soc., A, Vol. 100 (1921).

the same order as that obtained by Lambert.* In the absence of an accurate knowledge of the law of variation, a closer comparison is hardly possible.

In another experiment precipitated silica was heated very strongly, and this reduced its activity at atmospheric pressure. When used in a 3-litre vessel as in the other case, the factor obtained at first was about 200. As it was thought that moisture had been introduced accidentally during the injection of air, the apparatus was dried carefully and the experiment repeated. The factor then was about 900. There is little doubt that the lowness of this figure was due to partial deactivation produced by the strong preliminary heating.

In all the experiments the inner envelopes and the silica, which was placed in an internal capsule, were heated to 100° C. only during evacuation, and the factors obtained are those which correspond to these conditions. Copper itself appears to act as an adsorbent, and the factors are perhaps not strictly comparable with those found for adsorbents placed in glass vessels only and heated strongly during evacuation. (In the following cases the adsorbent was in its normal position in an internal capsule.)

(E) *Rate of Improvement of the Vacuum.*

(1) The pressure of the gas in the evacuated space of a Dewar vessel rises at once when air is admitted, and so does the rate of evaporation. These rises are both followed by a fall, which is rapid at first, and then slows down gradually, as a new state of equilibrium is approached. The effect of two successive injections of dry air in the case of a 5-litre vessel tested in October, 1919, is shown in Fig. 4. The first (20 c.c. at N.T.P.) caused the rate to rise suddenly from 0.365 L/M to 4.73 L/M, the rate ultimately obtained (18 hours later) being 0.75 L/M. The second (10 c.c.) produced a sudden rise from 0.77 L/M to 4.76 L/M, the final rate (19 hours after second injection) being 1.02 L/M.

The variations of the gauge reading are shown also, but while the rate of evaporation is varying the neck losses are not constant and the change in pressure does not give a measure of the change in the total rate of loss. Another complication is due to the fact that just after injections the pressures may be so high that they are no longer proportional to the gas conductivity. Further, unless the gauge is connected to the vessel by a short wide tube, its readings at any instant will not necessarily give the pressure in the vessel at that instant.

(2) Subsequent experiments made with vessels containing activated silica gave similar results, but much smaller injections were required.

Thus, in the case of one 3-litre vessel, 5 grammes of commercial precipitated silica was used, and two injections of dry air, each of about 0.5 c.c. (N.T.P.) were made. Equilibrium was approached more quickly than in case (a) Fig. 5.

(3) The effect of putting liquid oxygen into an evacuated 3-litre vessel containing silica is shown in Table III. Such a case is important because it illustrates the normal

TABLE III.

Evaporation Rate in L/M... ..	1.07	0.81	0.696	0.629	0.592	0.555	—	—	0.545	0.526
Minutes	5	10	15	20	25	30	35	45	48	60
Pressure in mm. $\times 10^{-4}$...	16.5	12.5	8.87	7.33	5.93	—	4.69	4.69	—	4.69

NOTE.—Minimum Rate was 0.33 L/M.

* Report of the Oxygen Research Committee, Department of Scientific and Industrial Research, 1923, paragraphs 81/86.

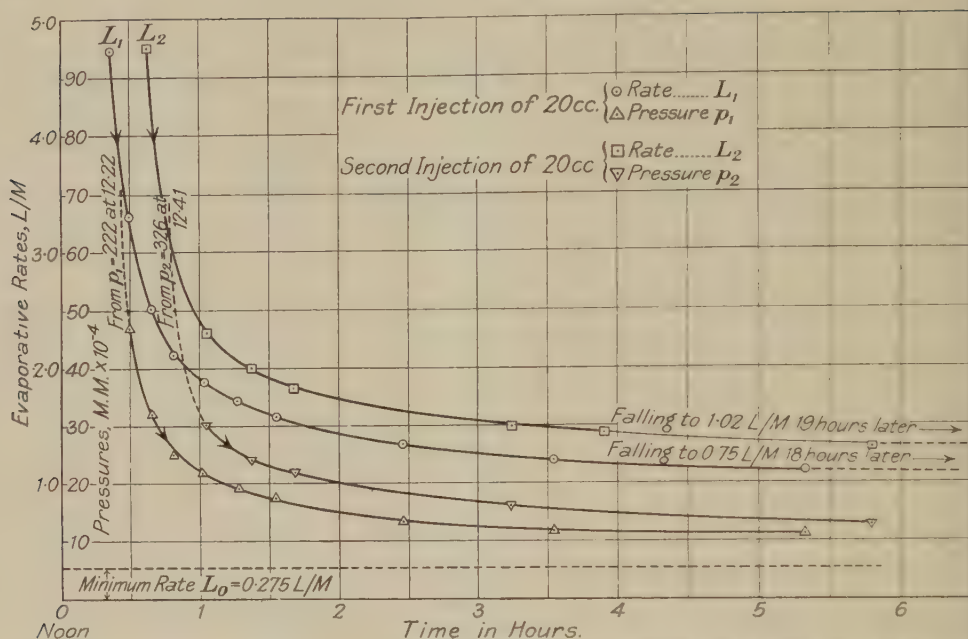


FIG. 4.—5 LITRE CONTAINER WITH CHARCOAL ADSORBENT. EFFECT, ON RATE AND PRESSURE, OF ADMITTING AIR.

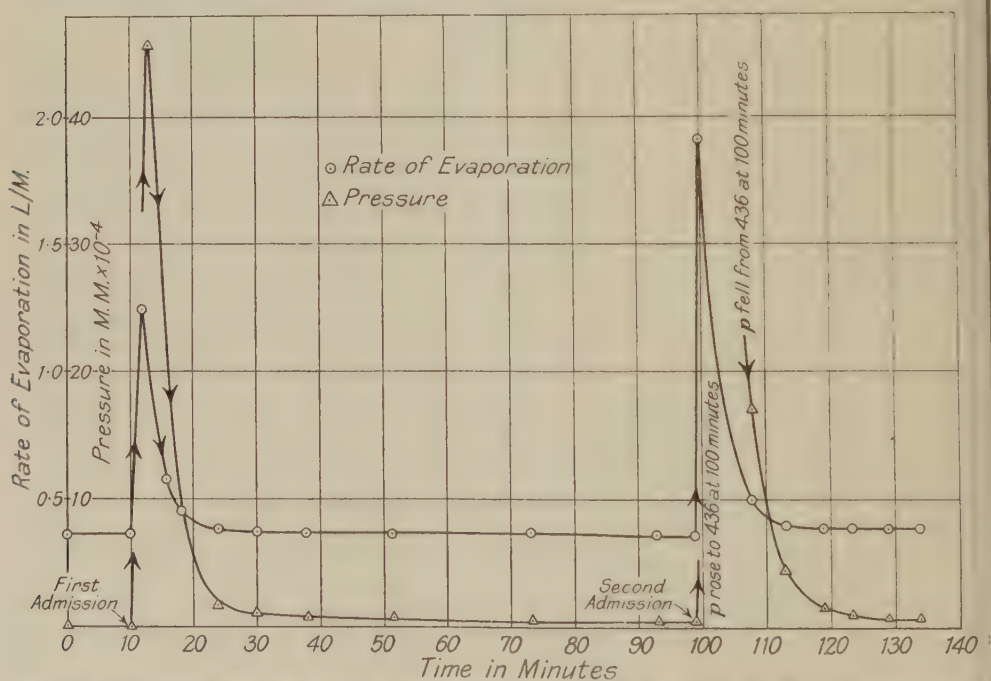


FIG. 5.—3 LITRE CONTAINER WITH SILICA ADSORBENT. EFFECT, ON RATE AND PRESSURE, OF ADMITTING DRY AIR.

At time, 10 minutes 0.48 c.c. admitted.

" 99 " 0.52 c.c. "

effects in a sealed vessel which has just been filled. As the inner envelope has to be cooled down, there is a very heavy initial delivery of cold vapour, and at first the inner neck is cooled strongly. Wetting of the neck may occur while filling is going on, and at first the neck losses are very small. Some time must elapse, therefore, before the neck recovers and the conditions get steady.

(4) The changes of rate just after a permanently sealed vessel has been filled are shown in Table IV, two cases having been taken. One case of special interest is that of a 5-litre vessel with no adsorbent.

TABLE IV.

Evaporative Rate in L/M .	Minutes after Filling completed.	Total Delivery in Litres.	Minutes after Filling completed.
	<i>First</i>	<i>Vessel.</i>	
9.7	.0	0	0
8.26	.7		
6.85	2.1	21.2	2.7
6.04	2.7		
4.93	3.9	33.3	5.1
4.07	5.1		
3.72	5.7	39.7	6.9
3.32	6.2		
2.99	6.9	44.4	8.7
2.64	7.7		
2.30	8.7	51.0	12.2
2.04	9.7		
1.76	10.8	55.8	15.8
1.50	12.2		
1.29	13.9	60.3	20.2
1.14	15.8		
1.02	17.8	99.8	66.5
.923	20.2		
.872	22.7		
.835	25.3		
.810	28.0		
.806	30.9		
.795	33.7		
.795	36.7		
.793	39.5		
.785	42.6		
.789	45.5		
.788	48.5		
.787	51.5		
.787	54.5		
.789	57.5		
.781	60.4		
.781	66.5		
	<i>Second</i>	<i>Vessel.</i>	
5.7	0	0	0
3.31	2	5.7	2
1.44	3	8.08	3
0.64	5	10.16	5
0.46	15	15.66	15
0.413	30	22.15	30
0.408	40.5	26.46	40.5
0.406	50	30.36	50
0.406	57	34.06	57

Curves of this type, taken over a period of one hour after filling, give useful information regarding the state of a vessel and the activity of the adsorbent. The total loss during the "settling-down" period may be found by a counter on the spindle of the meter, or by plotting the time/rate curve, and integrating. Measurement by loss of weight over so short a period is not accurate.

(F) *Rise in the Rate of Evaporation.*

(1) In 1919 some new 5-litre vessels were tested soon after evacuation, and the rates of evaporation measured. Six months or more afterwards these had risen so much that a second evacuation was necessary. This was carried out, but although there was a considerable reduction, the initial values were not reached. Hence the rise in rate could not have been due entirely to deterioration of the vacuum, and the vessels were therefore opened. The polished surfaces were found to be coated with an almost invisible layer of dust and oil. This was merely wiped off, and the vessels were at once put together again and evacuated. As shown in the annexed table, the rates were then as low, or lower, than they were initially:—

TABLE V.

Vessel No.	"Evaporative Rate" (L/M).			
	Initial.	At End of Period.	After Second Evacuation.	Third Evacuation after Cleaning.
1	0.27	0.47	0.36	0.26
2	0.24	1.65	0.30	0.24
3	0.26	0.80	0.41	0.24
4	0.24	0.60	0.36	—
5	0.33	0.56	0.36	0.24

It was found that the admission of 20 c.c. of air to No. 3 changed the rate from 0.41 to 1.83 L/M. When the same amount of air was admitted to No. 5 the rate changed from 0.36 to 0.65 L/M. These differences were due to variations in the adsorptive powers of the charcoal. When measured they were all found to be very low, but that from No. 5 was much better than the other.

(2) By evacuation at 100° C. the "rate" of a new 3-litre vessel examined in 1920 was reduced from 1.44 L/M to 0.62 L/M. The inner surfaces were found to be coated with polishing powder and charcoal dust. "Pockets" of the powder left after buffing had not been removed, and dust had come out of the charcoal, which was held in position by coarse gauze. After the surfaces had been buffed and a dust filter fitted, the minimum rate was 0.39 L/M.

(3) About two years after a 1-litre vessel had been evacuated the rate was 0.67 L/M (one hour after filling). After a second evacuation the minimum rate was about 0.38 L/M. Dry air was then admitted until the rate was 0.65 L/M. The pressure was then about 12×10^{-4} mm. mercury. Assuming that after the two-year period the residual gases were air, the pressure of those gases when the vessel was in use was just over 12×10^{-4} mm. mercury—that is, it was of the order of 1/1,000 mm.

IV. SEPARATION OF RADIATION AND NECK LOSSES. EMISSIVITY.

The separate evaluation of R and in N equation (4) is rather difficult, because the neck losses are not due to simple conduction only. Heat can reach the liquid via the neck in several ways, viz. :—

- (a) By conduction down the metal of the inner neck.
- (b) By gas conduction between the inner and outer necks.
- (c) By radiation.
- (d) By direct conduction and convection from the atmosphere to the liquid via the column of vapour.

Of these (a) is the most important ; and if the neck is long and narrow (d) is probably negligible. If the vessel is well evacuated (b) is very small. These variables are not all independent, and there is a complication due to abstraction of heat from the inner neck by the cold vapour. In consequence of this the neck losses are a function of the rate of gaseous delivery. It is possible to calculate them if certain assumptions are made,* but experimental determinations only are dealt with here.

Method 1.—Effect of varying the sectional area of the neck metal.

This method is described in Papers by Banneitz, Rhein and Kurze† and Briggs.‡

The rate of evaporation having been observed, a long, closely-fitting tube of the same material as the inner neck is pushed into that neck, forming a lining to the whole of its inner surface. The rate of evaporation finally attained is noted, and the neck losses deduced by a simple calculation.

Unfortunately, the conditions are not simple. Insertion of the liner not only changes the effective area of the neck, but alters its thermal state also, because of the increased flow of cold vapour. The calculation does not take this change of the conditions into account and can hardly give an accurate result. What the method actually gives is the rate of evaporation which will be obtained if the neck is replaced by one made of thicker metal.

Method 2.—Effect of Shortening the Neck.

It is important to find what increase will occur in the rate of evaporation if the neck of a given vessel is reduced in length. Comparisons made between vessels with long and with short necks are not of much value unless care is taken to secure equality in the radiation losses (a matter of some difficulty), especially in large vessels with slender necks. Further, samples of nickel-silver or cupro-nickel vary considerably in hardness and in electrical and thermal conductivity, and for this reason it is preferable to cut both inner necks from one piece of uniform tubing. If practicable, both vessels should be placed in one water bath with the evacuated spaces connected by a pipe.

The author prefers to use one vessel only, and to vary the effective length of its neck in one of two ways :—

- (a) A long thick copper tube or sleeve, which fits the inner neck, is pushed a

* Hogg, "A Note on the Conduction of Heat down the Necks of Metal Vacuum Vessels containing Liquid Oxygen," Trans. Faraday Society, No. 59, Vol. 20, Pt. 2, Nov. (1924)

† "Investigations with regard to the principles of Construction of Containers for the transport of Liquid Gases," (translation) Annalen der Physik, 4th Series, Vol. 61 (1920).

‡ "An Experimental Analysis of the Losses by Evaporation of Liquid Air contained in Vacuum Flasks," Proc. Roy. Soc. Edinburgh, Vol. 41, Pt. 2, No. 10 (1921)

certain distance into it, thereby producing a thermal short-circuit of the part which it touches, and reducing the effective length by a known amount. To secure good contact the sleeve is first ground into the neck tube, and then split longitudinally in several places. (In one series of experiments, the thermal conductance of the sleeve per linear centimetre was about 40 times that of the neck tube, and the fit was such that it was difficult to remove the sleeve.)

(b) The inner and outer necks are connected thermally by a short brass sleeve, which can be moved up or down, and clamped in any position (Fig. 6). The sleeve

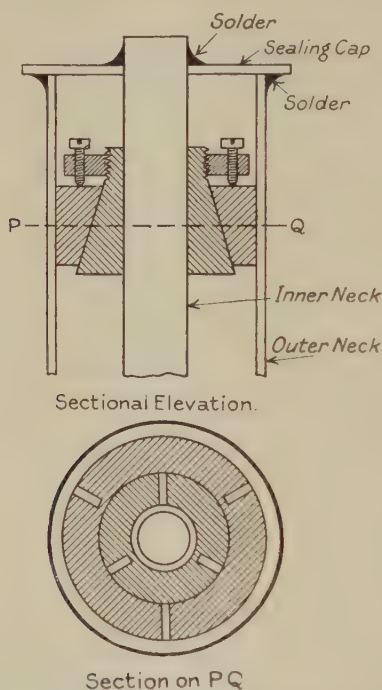


FIG. 6.—METHOD OF VARYING THE EFFECTIVE LENGTH OF THE NECK.

consists of male and female coned elements, which are split longitudinally, and may be pulled together by set screws. The tops of the necks are sealed together by a soldered metal washer, and when this is removed the screws may be turned. When the rotation is such that the male component is pulled into the female, the latter expands, and its outer cylindrical surface grips the inside of the outer tube. At the same time the male component is compressed, and its cylindrical inner surface grips the inner neck. The effective length may thus be varied without opening the body of the vessel and altering the constants appreciably.

The relation between the effective length of the neck and the rate of evaporation in the case of a 3-litre vessel is shown in Table VI., the actual length of the inner neck being 20 cms. As might be expected, the graph flattens towards the right, and tends to approach a definite limit. Since an indefinite lengthening of the inner neck would decrease its conductance, but would not stop entry of heat by radiation and gaseous

conduction, this limit does not give quite an accurate measure of the heat which enters by the body only.

TABLE VI.

Rate of evaporation in L/M ...	0.72	0.53	0.43	0.38	0.325	0.3*
Effective length of neck in cm. ...	3	5	8	10	15	20

Halving the effective length of the neck raised the total losses from 0.302 to 0.382 L/M , and the neck losses from 0.08 to 0.16 L/M —i.e., from 26 to 42 per cent.

Hogg,[†] from theoretical considerations applied to a 3-litre vessel with a neck 16.5 cms. long, concluded that the normal loss of 0.3 L/M would be raised in the corresponding case to 0.4 L/M , and that the neck losses would be 19 and 40 per cent.

Table VII. gives the relationship for a 25-litre container with a neck 30.5 cms. long, the vacuum being rather poor. Halving the effective length of the neck raised the total losses from 0.716 to 0.79 L/M , and the neck losses from about 0.006 L/M to 0.08 L/M , corresponding to about 1 and 10 per cent. Hogg's calculation for such a vessel when well evacuated gives total losses of 0.5 and 0.56, and neck losses of 0.02 and 0.08—i.e., 2 and 13 per cent. respectively.

TABLE VII.

Rate of evaporation in L/M ...	0.86	0.79	0.745	0.736	0.726	0.716
Effective length of inner neck in cm.	10.2	15.2	20.3	22.9	25.4	30.5

Method 3.—Measurement of Neck Losses by Cooling the Neck.

The charged vessel is placed in a bath and the "rate" noted. A cup which surrounds the upper part of the neck is then filled with liquid oxygen, and is replenished until the rate is again steady. Little or no heat can then pass down the inner neck by conduction, and the difference between the two observed rates gives an approximate measure of the neck losses. As it is difficult to cool the whole of the outer neck without cooling the body, the passage of heat into the inner neck by radiation and gas conduction cannot be stopped entirely. This transfer is not very great, however, and it is thought that the results obtained are not without value. Care must be taken to keep the temperature of the body of the vessel as constant as possible.

In the following examples the necks of all the vessels were nominally alike:—

(a) The evaporative rate of a 1-litre vessel fell gradually from 0.57 L/M to 0.336 L/M , giving a neck loss of 0.234 L/M .

Values of 0.232 and 0.221 were found in later experiments.

(b) Similar experiments with a 3-litre vessel gave the following results:—

TABLE VIII.

Date.	Initial rate.	Final rate.	Difference.
22/12/22	0.31	0.24	0.07
27/3/23	0.322	0.248	0.074

* Tends to approach a lower limit.

† "A Note on the Conduction of Heat down the Necks of Metal Vacuum Vessels containing Liquid Oxygen," Trans. Faraday Society, No. 59, Vol. 20, Pt. 2, November (1924).

(c) A 5-litre vessel with no adsorbent was evacuated in July, 1921, and its rate was found to be rising gradually on account of the steady rise in the pressure of the residual gases.

On 6/1/23, the initial and final rates were 0.77 L/M and 0.74 L/M, giving a neck loss of 0.03 L/M.

The low value of the neck losses in (c) is almost certainly due to the cooling action of the heavy flow of vapour, the additional effect of the liquid in the cup not being very great.

As the high value of both neck losses and rates of evaporation in (a) seemed anomalous the vessel was opened. The electrical resistance of the inner neck was abnormally low, and the thermal conductance was higher than usual. The high rates of evaporation were due partly to defective polish and partly to poor vacuum. Also, as the shells were cylindrical, with rounded ends, the ratio of surface to volume was rather high.

Method 4.—Neck and Radiation Losses, Emissivity.

As the amount of heat transferred by radiation between two polished surfaces which differ in temperature depends upon the emissivities and as these may vary with the wavelength, there will be some uncertainty if the law of variation is not known. In calculations relating to the Dewar vessel it is therefore desirable to use data obtained by experiment on an actual vacuum vessel, in order to ensure similarity of conditions.

It can be shown* that the amount of heat transferred by radiation in a Dewar vessel is approximately equal to—

$$A \times \frac{E}{2} \times 10^{-2} \text{ calories per second,}$$

where A is the area of the inner shell in square centimetres, and E the emissivity of the inner surface of the outer shell at some definite temperature, say, 20 °C. (The emissivity of a "black body" is taken as unity.) Hence, if the latent heat of liquid oxygen is 51 calories per gram, the rate of evaporation R , due to radiation only, will be

$$\begin{aligned} R &= A \times E \times 0.35 \text{ grams per hour,} \\ &= A \times E \times 0.00423 \text{ litres of gas per minute (N.T.P.).} \end{aligned}$$

(since 1 gram per hour corresponds to 0.012 litre of gas per minute).

$$\text{Hence,} \quad E = 236 \times \frac{R}{A} \quad \dots \dots \dots (8)$$

(R being in litres per minute).

In a well-evacuated vessel the only losses of any importance are the radiation and neck losses.

$$\therefore E = 236 \frac{L_0 - N}{A}, \quad \dots \dots \dots (9)$$

where L_0 is the observed rate of evaporation.

In determining E by this method the vessel should have a large body and a

* Report of the Oxygen Research Committee, Department of Scientific and Industrial Research, 1923, paragraphs 29/37.

long slender inner neck of thin material. L_0 will then be large, and the flow of vapour will make N small. Serious errors may be made if a small vessel with a short neck is used, or if the vessel is of a badly conducting material such as glass, and is only partially full.

Samples of glass differ widely in physical characteristics, and variations of temperature lead to changes in the conductance.

If the body of the vessel is made of a bad conductor there may be an appreciable temperature gradient between the base of the inner neck and the surface of the liquid. This may lead to complications, and render a reasonably accurate determination difficult or impossible.

Examples.

(a) *Obtaining E and R .*—After a prolonged evacuation a 25-litre container was losing vapour at the rate of 0.44 litre per minute, $A=3970$.

$$\therefore E=0.0595 (0.44 - N).$$

From preliminary experiments it was concluded that N was not greater than $0.04 L/M$ nor less than $0.02 L/M$, giving for E the values 0.0238 and 0.0262, with a probable value of about 0.0244.

This gives the radiation loss $R=0.41 L/M$.

The value given for the emissivity of copper by Hagen and Rubens* is 0.16; but, apart from possible variations in the nature of the radiation, constants obtained for pure metals are not necessarily applicable to commercial ones, which have been spun, pressed or partially annealed. The polish reached during manufacture is not so high as that obtainable with a small area which is not part of an actual vacuum vessel; and the emissivity may be affected by the removal of adsorbed gases during evacuation.

(b) *Finding N and R .*—The values of E or of R obtained by experiments on a large vessel may be used for finding the losses on a smaller vessel, in which N is not small in comparison with R or L_0 .

Thus in one 3-litre vessel tested

$$L_0=0.222 L/M, \quad A=1,142 \text{ sq. cm.}$$

$$N=L_0 - \frac{EA}{236} = 0.104 L/M \text{ and } R=0.118 L/M.$$

Method 5.—Change in the Neck Losses Due to a Variation in the Rate of Gas Flow.

The rate of evaporation L_0 is raised to some steady value L_1 by sending a current through a coil immersed in the liquid oxygen and the input in watts noted. The current is then increased until the rate of evaporation becomes steady at another value L_2 , and the watts are again measured.

Let	N_0, N_1 and N_2	=neck losses at deliveries L_0, L_1 and L_2 .
„	W_1 and W_2	=losses due to the watts.
„	w	=the losses due to the leads.
„	R	=losses due to body radiation.

* Report of the Oxygen Research Committee, Department of Scientific and Industrial Research, 1923, Paragraph 37, Table 4.

Also, for a moment after the current has been cut off, the neck of the small vessel remains in the thermal state which corresponds to a delivery L and neck loss N .

Hence $l_0 = r + N + w$ (21)

... from equation (18)

$$N = (l_0 - w) \left(\frac{A}{A - a} \right) - L \left(\frac{a}{A - a} \right) \quad \text{. (22)}$$

W may be found as before; and w by measuring, by a reflecting flow meter, the small rise produced in the rate of evaporation when the coil, with no current flowing in it, is put into the liquid. The slight increase in the flow of cold vapour will have very little effect on N , but before the coil is immersed it should be cooled in liquid oxygen.

The loss w may be reduced by using one lead only, and completing the circuit by the inner vessel and neck.

Since N is usually small, and in equation (18) is given as a difference between two terms, a small error in measuring either may lead to a considerable percentage error in the result. For this reason it is preferable in some cases to find W by a separate experiment, the same heating coil being used. The latent heat need then not be known, and if the same meter is used for measuring both L and W the error in N will be reduced.

Equation (18) may be written

$$N = L - \frac{(W + w)}{1 - \frac{r}{R}} \quad \text{. (23)}$$

If the inner surfaces of the vessels are not polished equally well, or if the external temperatures differ slightly, $\frac{r}{R}$ will not be equal to $\frac{a}{A}$. The error may be reduced by

making $\frac{r}{R}$ small. One vessel therefore should be much smaller than the other.

In experiments on radiation losses w may be eliminated by passing the current through compensating leads attached to a duplicate or dummy coil in the larger vessel. The leads are short-circuited near the bottom, and the coil has a break in it. w will then be the same for each vessel, and we get

$$\frac{R}{A} = \frac{W}{A - a}$$

which involves only W and the difference between the areas. Also, from equation (9)

$$E = 236 W \left(\frac{1}{A - a} \right) \quad \text{. (24)}$$

A somewhat different case is that of vessels which have equal necks of the same material but bodies of different materials. The heater is used to bring the lower delivery L_2 up to the higher L_1 , and we find

$$R_1 - R_2 = W - (G_1 - G_2) \quad \text{. (25)}$$

If G_1 and G_2 are negligible

$$R_1 - R_2 = W \quad \text{. (26)}$$

Thus, if the radiation loss of one vessel is known that of the other may be found, and the emissivities compared. The "cut-off" method may be applied here also. If the relative sizes of the bodies have been so adjusted that $L_1 = L_2$ no heater will be required. The neck losses will then be equal and $R_1 = R_2$.

Hence
$$\frac{E_1}{\bar{E}_2} = \frac{A_2}{A_1} \quad \dots \dots \dots (27)$$

where the A 's are the radiating areas.

If the bodies are equal and the evacuated spaces are in communication, then $G_1 = G_2$ and equation (26) still holds.

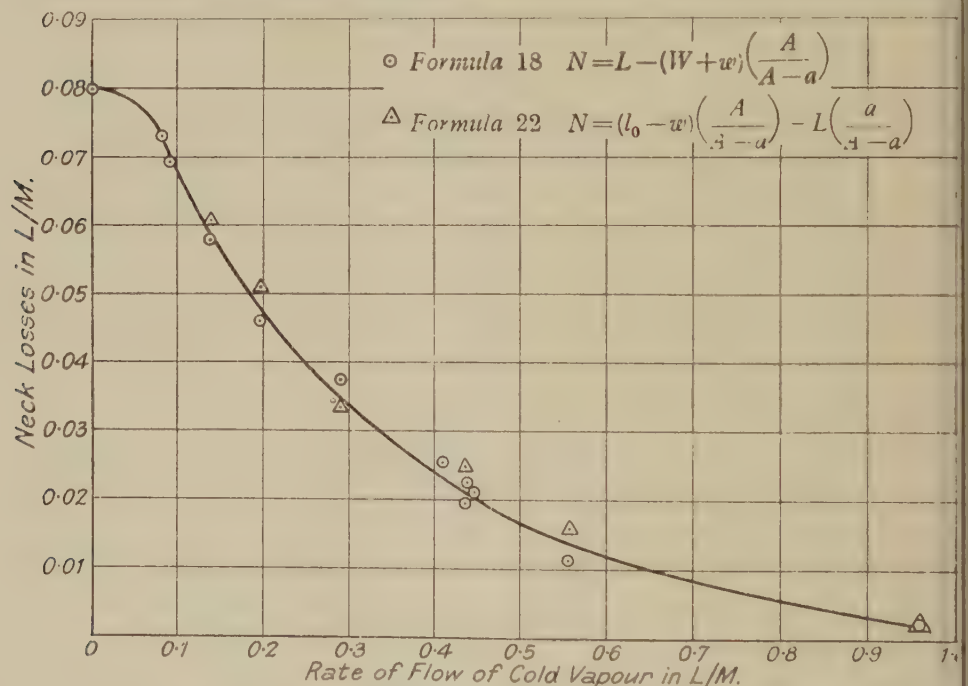


FIG. 7.—EFFECT OF FLOW OF COLD VAPOUR ON NECK LOSSES OF 25 LITRE CONTAINER. (Two-vessel Method).

Errors due to imperfect evacuation will therefore be eliminated, or at least reduced.

In all the following examples the same small supplementary vessel was used. The diameter of the inner shell was 5.3 cms.; and both shells were so designed that any standard inner or outer neck could be soldered to them.

(a) The neck losses of a 25 litre container at various rates of gas flow are shown in Fig. 7; and, as will be seen, they fell from 0.073 L/M to 0.004 L/M when the total delivery was increased from 0.082 L/M to 0.96 L/M.

Rather higher values were given by equation (22) ("cut-off" method).

A rough calculation based on the mean conductivity of the neck metal, and neglecting radiation into the neck, gave about 0.03 L/M as the probable value which

N would have if none of the evolved vapour passed through the neck, a condition which obviously cannot hold for an actual vessel. As the graph, however, shows the relationship between the amount of heat transmitted by a definite piece of neck tubing, and the flow L of cold vapour through it, quite irrespectively of how the flow has been produced, the flow of cold vapour may be supposed to be cut off or put equal to zero.

On plunging the body of the small vessel into liquid oxygen the immediate fall in the rate was $0.01 L/M$, which gives r approximately. A greater fall took place later as the outer neck became progressively cooler by direct conduction of heat downwards.

(b) Other examples are shown in Tables IX to XI.

TABLE IX.—Vaporizer Neck Tubing. Losses at Various Deliveries.

Rate of flow in L/M .	Neck losses, N , in L/M by method			
	6 (Eqn. 18).	6 (Eqn. 22).	3.	4.
0.175	0.138	0.128
0.218	0.122	0.112
0.222	0.104
0.234	0.116	0.106
0.267	0.098	0.088
0.32	0.07	...
0.77	0.03	...

Had the vapour not cooled the neck value of N , by a rough calculation as in Method 6, paragraph (a), would have been about 0.16 to $0.2 L/M$.

TABLE X.—Radiation Losses of Various Vessels.

Vessel.	Radiation Loss in L/M .	
	Method 6.	By cooling body.
25 litres	0.423	...
5 "	0.172	...
3 "	0.121	...
1 "	0.065	...
Supplementary	0.0097	0.01

TABLE XI.—Radiation Loss of 3 Litre Vessel by Method 6. Emissivity.

By experiment on small vessel and vessel of capacity.	Equation 18	...	Equation 22.	...
	R .	E .	R .	E .
25 litres	0.121	0.0251	0.121	0.0251
5 "	0.119	0.0246	0.126	0.0260
3 "	0.118	0.0244	0.128	0.0265

Mean value of $E = 0.0253$.

By method (4) $R = 0.118 L/M$.

$E = 0.0265$.

DISCUSSION.

Prof. O. W. RICHARDSON said that as a rather heavy consumer of vacuum flasks he had often wondered how much heat is lost by conduction along the neck, and it was very satisfactory to know that such loss is inconsiderable.

Mr. G. R. D. HOGG said that the Oxygen Research Committee had been faced with the absence of any data for determining the relative importance of the various ways in which heat is lost from vacuum vessels, and the present research was undertaken at their instance. Some idea of the practical difficulties overcome by the author could be gathered from the fact that, in one flask, 7 ft. of soldered jointing had to be unmade and remade from time to time. He thought that the author's experiments, confirmed by some calculations for which he was himself responsible, had gone far towards providing satisfactory information for the use of designers of flasks.

Dr. G. W. C. KAYE said he understood that great difficulty is experienced in "outgassing" the adsorbent which is employed for the purpose of keeping up the vacuum, as the temperature cannot be raised very high without damaging the soft-soldered joints. Would not silver-soldering or brazing be a better method of jointing?

AUTHOR'S reply (communicated): I have been aware for a long time that a metal surface cannot be out-gassed properly by heating to so low a temperature as 100°C. I have made a practice of heating the outer shells during evacuation by applying a flame cautiously; but this cannot, of course, be done to parts near the soft-soldered joints. Unfortunately, brazing or silver-soldering makes the metal too soft to stand reasonably rough usage, and it is difficult to see how serious tarnishing of the metal can be avoided during assembly. A special process would have to be developed; and this might be difficult and probably would be expensive. It must be remembered that the adsorbent is put into the vessel with the express object of making the initial evacuation easy and adsorbing gases which may diffuse gradually from the metal into the evacuated space. Vessels properly evacuated at 100°C. maintain low rates of evaporation for long periods, and re-evacuation is neither difficult nor costly. Some years ago the Germans experimented with welded vessels, but do not appear to have adopted the process commercially. Both German and French vessels now on the market are, I believe, made with soft-soldered joints. The reason is probably financial.

DEMONSTRATION OF THE APPLICATION OF THE PIEZO ELECTRIC PROPERTIES OF A ROCHELLE SALT CRYSTAL AND THE TRI-ELECTRODE VALVE TO THE DETERMINATION OF IMPACT STRESSES IN GRANULAR MATERIAL.

By J. J. HARTLEY, *M.Eng., M.Sc., A.M.I.C.E.*, and R. H. RINALDI.

THE distribution of stress in granular material under a continued load with the essential minimum of movement in the measuring apparatus has been determined by several observers, including Goldbeck (*Proc. Am. Soc. for Test. Mat.*, 1917), Shaxby and Evans (*Trans. Far. Soc.*, 1923); but the apparatus employed by these investigators does not appear to be adapted for the investigation of instantaneous loads.

For the purpose of the investigation of this problem the present instrument has been designed. The apparatus consists of a Rochelle salt crystal which is subjected to axial compression by means of three springs, this pressure remaining constant throughout the experiment. The variation in electric potential which is made use of is obtained by the application of torsion; for, as noted by Nicholson, the piezo-electric effects in the case of Rochelle salts are more pronounced when the crystal is subjected to torsion than are those obtained by axial loading.

One pole of the crystal—that is to say, the negative—is connected to the grid of a tri-electrode valve, and modifies the grid bias according to the amount of the torsion. The relation between these two factors is not a linear one, but gives when plotted the same type of curve as the ordinary valve characteristic, and the initial tension is so adjusted that with the actual torsion applied the slope of this applied torsion, grid potential curve is a maximum. In the same way the permanent grid bias is chosen so as to give a maximum slope to the anode current, grid potential curve.

The other pole of the crystal is earthed, and the effect is thus similar to that obtained when a charged ebonite rod is applied to the grid.

The chief difficulty in the satisfactory calibration of the apparatus has been found to be the surface leakage of the crystal, which varies to a considerable extent with the atmospheric conditions.

Coating the crystal with varnish and paraffin wax has been tried, but up to the present with only moderate success.

The sensitivity of the electrical mechanism, when using a Marconi R type valve with 40 volts high tension and no permanent grid bias, is about 100 micro-ampere change in plate current per 100 grams increase in load under the best atmospheric conditions. This sensitivity could be easily increased if necessary by increase in the spring tensions, or by more complete drying of the crystal; but such increased sensitivity is only obtained at the expense of the mechanical strength.

DEMONSTRATION OF SOME SURFACE TENSION PHENOMENA

By EDWIN EDSER.

(a) It is well known that when a water surface is touched with an oily needle the small quantity of oil applied spreads rapidly, as may be shown by covering the surface with lycopodium powder. In the present instance it was shown that a hydrocarbon oil does not spread in this way if it be perfectly pure, whereas the slightest touch of a needle fouled with oleic acid produces an immediate effect.

(b) A quantity of pure paraffin oil was floated on water, the interface being shown in optical projection by means of a layer of freshly-prepared aluminium powder which rested on the water. A drop of oleic acid from a capillary tube was allowed to sink through the paraffin, and on reaching the interface it immediately spread with great rapidity, carrying the aluminium powder with it.

(c) It might be expected that a spot of pure paraffin floating on water would arrange itself so that its upper and lower surfaces meet at an acute angle, their line of inter-section with one another being coincident with their line of intersection with the water surface. It was shown by optical projection, however, that the edge of the spot is "tucked under," the water surface intersecting the lower surface of the spot along a line below the latter's maximum horizontal cross-section. Fouling of the water surface with a small quantity of oleic acid causes the paraffin to collect itself into rounded drops.

FURTHER DEMONSTRATION OF SURFACE TENSION PHENOMENA

By Prof. C. R. DARLING.

THE experiments shown related to the Paper by R. S. Burdon on "The Spreading of One Liquid Over Another," read before the Society on December 11.

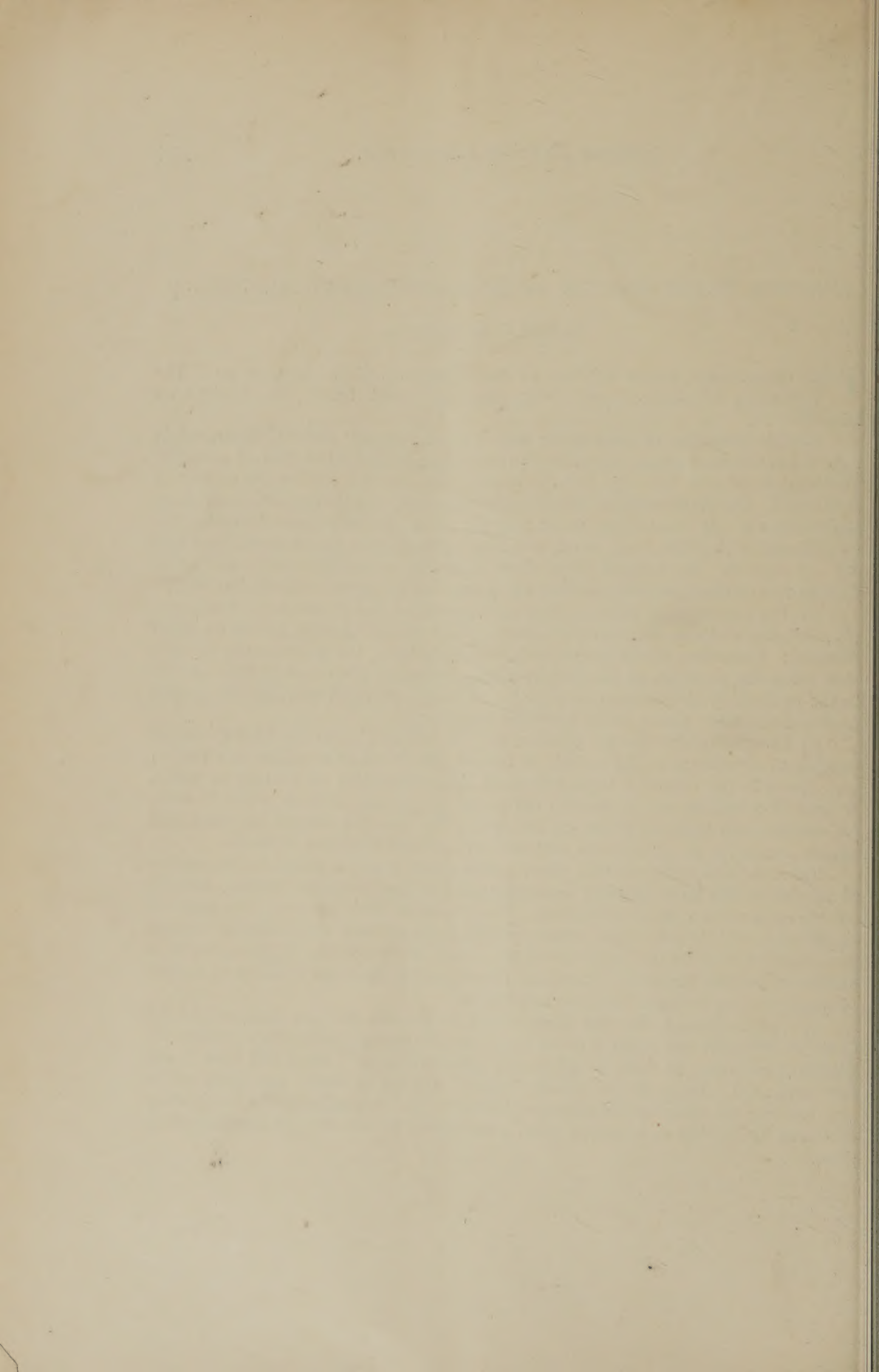
(d) The spreading of pure water over a clean mercury surface, illustrated in Figs. 3-5 of Burdon's Paper, was shown to be identical with that of olive oil on water. The beaded ridge at the edge and the holes in the internal portion are present in both cases. The water surface had a diameter of 9 cms., and the drop of oil measured about 0.05 c.c. It was further shown that the water surface beyond the main drop was covered with a thin layer of oil, and that a second drop placed outside the first did not expand. The original drop, after expanding, gradually shrank, and broke up into two or three portions, each of which assumed a permanent lenticular shape.

(e) The formation of holes in films after spreading was shown to be a common phenomenon, and was illustrated by placing drops of the following liquids on water surfaces: Quinoline, nitrobenzene and dimethylaniline, the after-results in each case being the partition of the film by canals spreading from hole to hole, ending in the production of numerous globules; and tar-oil, in which case the film heaped up round the holes, giving rise to a cellular formation.

(f) In order to illustrate a suggestion that the changes in the film after spreading are due to alterations in the interfacial tension, the result of changing this tension was shown in the case of a large globule of light lubricating oil floating on water. A drop of quinoline was allowed to fall on to the globule, through which it sank. On reaching the junction of the oil and water the quinoline altered the interfacial tension, when the oil globule was shattered with almost explosive violence.

The view was expressed that when a drop of one liquid is placed on the surface of another, a thin layer (possibly monomolecular) flashes across the surface, drawing out the main mass of the floating drop. The expanded drop, however, is in unstable equilibrium, and the interfacial tension gradually asserts itself and gradually restores the distorted drop to the lenticular shape, which is then stable, or gives rise to a number of smaller globules. The holes formed in the films are evidence of a state of strain existing between the boundary ridges.

It was mentioned that the ridge stated by Burdon as being first noticed by Osborne Reynolds was referred to by Prof. James Thomson in his Paper before the British Association in 1855, in which the phenomenon of "tears and wine" was first explained. Between the falling "tears" a ridge of liquid was observed to rise, forming the material for subsequent drops. This is similar to the rising ridge described by Burdon as occurring when water drains from a sheet of perfectly clean glass.



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